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JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Rays in the Solar Spectrum produced by Atmospheric Absorption. By L. THOLLON (*Compt. rend.*, **91**, 520—522).—By means of a spectroscope of exceptional power, the author has accurately measured and laid down the positions of a number of lines in the telluric groups B, D, and α of Angström. Thus, between the two D lines he has ascertained, with a possibility of error not exceeding about the 150th part of the whole interval, the positions of twelve lines, of which at least ten are of telluric origin. R. R.

Luminous Spectrum of Water. By HUGGINS (*Compt. rend.*, **90**, 1455—1456).—The flame of hydrogen burning in air, or of the oxyhydrogen light, gives only a faint continuous spectrum, but on the photographic plate a group of lines is obtained in the ultra-violet, of which the most refrangible are λ 3062 and λ 3068. This spectrum, doubtless that of water, is also seen when coal-gas is substituted for hydrogen in the oxyhydrogen flame, in the alcohol flame, and in the electric spark when moisture is present either on the electrodes or in the atmosphere. In the two former cases, the spectrum of carbon is also seen.

A list of the wave-lengths of the lines of the spectrum of water is given. L. T. O'S.

Inversion of Photographic Images by the Prolonged Action of Light. By J. JANESEN (*Compt. rend.*, **90**, 1447—1448).—In taking photographs of the photospheric granulations of the sun, by exposing the plate for one-thousandth of a second (the time of exposure differs with the state of the atmosphere and the nature of the

photograph required, but very rarely exceeds the above), or, in the case of plates prepared with gelatin and silver bromide, one twenty-thousandth of a second, a true negative image is obtained, those parts being dark which in reality are light. By continuing the action of the light, the image still remains negative, but loses its distinctness; then a point or neutral stage is reached when the developing solution reveals scarcely any image. Now by continuing the action of light, the negative is replaced by a positive image, in which the face of the sun is white and the spots black, as the disc is seen through a telescope. By still prolonging the action of the light, a second neutral stage is reached, which is the reverse of the former. This inversion of the image is due to the great radiant power of the sun.

L. T. O'S.

Optical Properties of Mixtures of Isomorphous Salts. By H. DUFET (*Compt. rend.*, **91**, 286—289).—The refractive index of a crystal formed of a mixture of two isomorphous salts varies with the composition in such a manner that the variation is proportional to the number of equivalents of one of the salts introduced into the mixture. If N is the index of the mixed salt, n and n' the indices of the component salts, p and p' the numbers of equivalents of the two salts—

$$N = \frac{pn + p'n'}{p + p'}.$$

In a previous paper, the author demonstrated this law for mixtures of nickel and magnesium sulphates; he has now verified it, by a more precise method, for mixtures of zinc and magnesium sulphates. The difference between the angle contained by the optic axes, as directly observed, and as calculated by the aid of the above law from the known composition of the mixtures, does not amount to more than two or three minutes. Details of the mode of observation and of calculation are given.

The author thinks it probable that the law is true of all isomorphous salts which have the same specific volume. J. M. H. M.

Development of Electric Polarity by Pressure in Hemihedral Crystals with Inclined Faces. By J. and P. CURIE (*Compt. rend.*, **91**, 294—295).—The authors find that with pyroelectric crystals the same effects are produced by the application and release of pressure as by cooling and heating, viz., the development of electricity of opposite polarity at the extremities of the hemihedral axis. In order to observe the effect, a slice of the crystal is prepared with parallel faces at right angles to the hemihedral axis. A leaf of tinfoil is then applied to each face, covered by a layer of sheet india-rubber, the whole placed in a vice, and the tinfoil connected with a Thomson's electrometer. The crystals experimented with were blende, sodium chlorate, boracite, tourmaline, quartz, calamine, topaz, dextro-tartaric acid, sugar, and Seignette salt. The effect of heat and pressure on this class of crystals is summed up in the following statement:—Whatever the determining cause, whenever a non-conducting hemihedral crystal with inclined faces suffers contraction, electric polarity

is developed; whenever it is dilated, electricity is also developed, but the polarity is reversed. J. M. H. M.

Researches on the Silent Electric Discharge. By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **91**, 281—283).—This paper is devoted to a description of the appearance presented by the luminous brushes (*pluies de feu*) produced in silicon fluoride, nitrogen, hydrogen, chlorine, oxygen, and carbonic anhydride, when these gases are placed in the annular space between the concentric tubes of A. Thenard's alternating discharge apparatus. The phenomenon is most brilliant in silicon fluoride at pressures above 5 millimetres. In all gases, it only appears at certain pressures, passing with increase of pressure into the electric spark, and with diminution of pressure into the uniform glow of a vacuum tube. Except at very feeble pressures, the phenomenon is accompanied by a noise like that made by the commutator of an induction coil. J. M. H. M.

Voltaic Cells. By A. D'ARSONVAL (*Compt. rend.*, **91**, 284—285).—The chemical action of a two-fluid cell does not entirely cease when the circuit is open, on account of the mixture of the two liquids, which gradually takes place by endosmose or diffusion. The author has succeeded in removing this defect by two methods, different in principle. The first method is founded on the property possessed by animal charcoal of withdrawing metallic salts from their solutions. This method answers best for cells without a porous diaphragm. If, for instance, a layer of powdered copper sulphate is covered by a layer of animal charcoal, and the zinc and exciting liquid placed on the top of these layers, as in an ordinary Callaud element, the zinc will remain unaltered for any length of time as long as the circuit is not completed. The internal resistance of the cell is increased by the layer of charcoal, but not more so than by the sand which is commonly used. The author has endeavoured to construct porous cells of animal charcoal, but without success.

The second method is a more general one, and consists in the employment of a depolarising liquid which forms a precipitate with the exciting liquid. This precipitate very soon forms an impermeable coating on the walls of the porous cell, which prevents the mixing of the liquids by diffusion. The precipitate must conduct electricity and be an electrolyte. An element formed of zinc in zinc chloride in the outer cell, and silver in silver nitrate in the porous cell, has an electromotive force of 1·5 volt and a very small resistance. A cheaper element, composed of zinc in zinc sulphate, with lead in lead nitrate, has an electromotive force 0·6—0·75 volt. Instead of a metallic salt, a base may be used as the precipitating agent. Thus, zinc in sodium hydrate, copper in copper sulphate = 1·5 volt; zinc in sodium hydrate, copper in ferric chloride = 2·4 volts. If potassium hydrate be used, the internal resistance is very great, but may be lessened by addition of sodium chloride or sulphate. J. M. H. M.

Electrolytic Experiments. By E. F. SMITH (*Ber.*, **13**, 751—754).—A black hydrated oxide, U_3O_4 , is precipitated, when a gal-

vanic current is passed through a solution of uranium acetate, formate, or nitrate. This reaction may be used for the quantitative separation of uranium from the alkalis and alkaline earths. Molybdenum, tungsten, vanadium, didymium, and cerium salts are not completely precipitated from their solutions by the galvanic current.

W. C. W.

Rise of the Zero Point in Mercury Thermometers. By J. M. CRAFTS (*Compt. rend.*, **91**, 291—293).—It is well known that the zero point of a mercury thermometer is lowered some tenths of a degree when the thermometer is heated to about 100°, whilst prolonged exposure to a much higher temperature causes an elevation of the zero point amounting to several degrees. The author's experiments refer to the latter phenomenon, and the results of repeatedly heating eight thermometers for periods of from 20 minutes to 12 days, at temperatures varying from 10° to 355°, are embodied in a series of tables. The numbers given in the tables are arbitrary, but the following are the conclusions drawn by the author:—

1. The zero point rises more rapidly in thermometers of lead glass than in those of glass free from lead oxide.

2. The change is much more rapid at the commencement, and probably tends towards a limit for a very prolonged heating at a fixed temperature.

3. The zero point, raised by prolonged heating at a high temperature, remains fixed at the new height when the instrument is kept at the ordinary temperature, and the effect produced by the high temperature renders the thermometer more stable under the influence of any inferior temperature.

The maximum effect shown in the tables is an elevation of 26·4° after heating the thermometer for an aggregate period of 263 hours at 355°.

J. M. H. M.

Variation of the Fixed Points in Mercury Thermometers.

By J. PERNET (*Compt. rend.*, **91**, 471—473).—In this note, the author discusses the experiments of Mills and of Crafts in connection with his own observations. For temperatures not greatly exceeding 100°, the following correction will be found to give nearly accurate results, even with thermometers of different glass, and which have been differently treated. The minimum zero corresponding to the temperature t° is either directly observed, or calculated by means of the formula

$$z_t = z_0 - (z_0 - z_{100}) \frac{t^2}{100^2},$$
 where z° is the zero point observed after long immersion in melting ice, and z_{100} the minimum observed immediately after the thermometer has been heated several times to 100°.

From observations made at the temperature t° , the minimum z_t is subtracted, and the value of the degree is taken as the hundredth part of the interval comprised between the 100° point and the zero observed immediately after the determination of the latter. The observation is then completely corrected for the displacement of the zero point.

J. M. H. M.

Defects of the Mercurial Thermometer. By J. M. CRAFTS (*Compt. rend.*, 91, 574—576).—The atmospheric pressure is not the cause of the elevation of the zero point which is observed in mercurial thermometers. This, and probably other irregularities in the indications of the instrument, are, in the author's opinion, to be explained only by changes in the molecular condition of the glass, by which its coefficient of expansion is altered. The author will shortly describe a new method of graduation intended to remedy these defects.

R. R.

Changes in Glass by Heating. By J. SALLERON (*Compt. rend.*, 91, 690—692).—Thermometers which have been exposed to high temperatures are sometimes found to give indications more than 8—10° from the truth. The paper describes changes produced in glass hydrometers by continued immersion in hot liquids. Their weight diminishes, their forms are changed by slight bulging or bending, they frequently crack in odd spiral-like lines, and sometimes they fly in pieces. The more alkaline glasses appear the most liable to changes of form.

R. R.

Influence of Temperature on the Distribution of Salts in Solution. By C. SORET (*Compt. rend.*, 91, 289—291).—The author tabulates the results of a number of experiments with solutions of potassium nitrate, potassium chloride, and sodium chloride. Homogeneous solutions of these salts of various degrees of concentration were introduced into long glass tubes, the upper ends of which were placed in a bath maintained at 78°, while the lower ends were cooled in water. After the lapse of from 10 to 56 days, the tubes were opened, and the upper, middle, and lower thirds of the solution were separately collected and examined. The general results are summed up thus:—

1. For all salts already studied, the concentration of the heated portion diminishes; that of the cool portion increases.

2. The difference which is established increases with the original concentration of the solution; and in the case of potassium chloride and sodium chloride, seems to be approximately proportional to the concentration.

3. In the case of solutions of alkaline chlorides of the same degree of concentration, the difference increases with the molecular weight.

4. The phenomenon appears to have no relation to the solubility curves of the salts.

J. M. H. M.

Reciprocal Displacements of the Halogen Elements. By BERTHELOT (*Bull. Soc. Chim.* [2], 34, 73—76).—The displacements of bromine and iodine by chlorine, and of iodine by bromine in their metallic combinations is in strict accordance with the thermochemical theory. The inverse displacements, although impossible under ordinary circumstances, are *à priori* possible under special conditions, such as are the dissociation of the primary combinations, the formation of secondary combinations, as the chloride and bromide of iodine, and combinations in multiple proportions as potassium tri-iodide or tribromide, the two chlorides of mercury, &c. The author has shown in the cases

of oxygen and chlorine combined with arsenic, and of oxygen and iodine with potassium, that these inverse displacements are possible, if in the formation of the secondary combinations a quantity of heat is evolved greater than that absorbed by the direct substitution in the primary combinations (this Journal, Abstr., 1879, 351). These secondary combinations can only interfere if the temperature of the reaction is below the limit defined by their dissociation coefficient. Potilitzin (*Ber.*, **9**, 1027; *ibid.*, **12**, 695, and 2369; this Journal, 1877, ii, 109; Abstr., 1879, 770; Abstr., 1880, 365) has observed the inverse but limited replacement of chlorine by bromine. This the author attributes to secondary reactions, such as the formation of iodate by the oxygen of the air in presence of moisture and alkalis or acids present in glass apparatus, and experiments are quoted in support of this view. In an atmosphere of pure and dry nitrogen, however, using porcelain vessels, when potassium chloride is heated with bromine, or potassium bromide with iodine, it remains unaltered. V. H. V.

Heats of Formation of the Oxides of Nitrogen and of Sulphur. By BERTHELOT (*Compt. rend.*, 1449—1455).—The author comments on the concordance between his results (this Journal, Abstr., 1880, 522) and the corrected results of Thomsen (*ibid.*, 603) on the heat of formation of nitrous oxide. The fact that the two results were obtained independently, and by different methods, the author considers a proof of the correctness of the numbers. Regarding the heat of formation of the equivalent of sulphur dioxide, $\frac{1}{2}\text{SO}_2$, the author's number, 34.55, is lower than any yet obtained, that obtained by Thomsen being 35.54. The author, to prove the correctness of his results, has repeated his experiments, and shows that the difference between his and Thomsen's results is due to the formation of a small quantity of sulphur trioxide when sulphur is burnt in oxygen. By estimating the amount of higher oxide formed, which, when 0.8 gram of sulphur was burnt amounted to 0.0019 gram, and eliminating this source of error, the heat of formation of sulphur dioxide was found to be 34.63. This confirms the author's previous result.

L. T. O'S.

Action of Dry Hydrogen on Anhydrous Haloid Salts. By POTILITZIN (*Bull. Soc. Chim.* [2], **34**, 85—86).—The chlorides and bromides of lead and cadmium are easily reduced when heated in a current of dry hydrogen, the reaction taking place at temperatures below the fusing points of the salt. These experiments, and the reciprocal displacements of oxygen and the halogens in metallic chlorides, which the author has previously established, are not in accordance with the theory of elective affinities, the work of which is measured by their relative heats of combination. V. H. V.

Cuprous Chloride. By BERTHELOT (*Bull. Soc. Chim.* [2], **34**, 76—78).—A continuation of the thermochemistry of cuprous chloride (*Compt. rend.*, **89**, 967—971; this Jour., Abstr., 1880, 208).

Heat of Solution.—The following determinations were made:—

$\frac{1}{2}(\text{Cu}_2\text{Cl}_2) + 22(\text{HCl} + 5\text{H}_2\text{O})$	absorbed	- 0.41	heat-units*
$\frac{1}{3}(\text{Cu}_2\text{Cl}_2) + 22(\text{HCl} + 5.5\text{H}_2\text{O})$	„	- 0.67	„
$\frac{1}{2}(\text{Cu}_2\text{Cl}_2) + 22(\text{HCl} + 12\text{H}_2\text{O})$	„	- 1.87	„
$\frac{1}{2}(\text{Cu}_2\text{Cl}_2) + 22(\text{HCl} + 128\text{H}_2\text{O})$	„	- 4.75	„

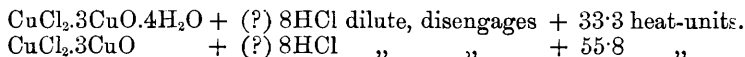
The last experiment was near the limit of dilution at which the salt begins to be precipitated. The author attributes the variation of the heat absorbed to definite compounds formed by hydrochloric acid, water, and cuprous chloride, in pairs, the nature of which varies with their relative proportions. The experiments show that it is incorrect to suppose that precipitates or substances insoluble, or nearly so, possess a definite and constant heat of solution without regarding the often complex chemical reaction induced by their solution.

Solubility of Cuprous in Cupric Chloride.—Cuprous chloride dissolves readily even in dilute solutions of cupric chloride, the green solution depositing a pale green oxychloride, probably identical with atacamite.

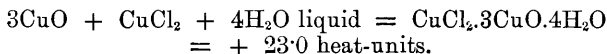
The *heat of formation of cuprous chloride* was measured by the conversion of cuprous into cupric chloride by barium or hydrogen peroxide and hydrochloric acid. The value deduced for $\frac{1}{2}\text{Cu}_2 + \frac{1}{2}\text{Cl}_2 = \frac{1}{2}(\text{Cu}_2\text{Cl}_2)$ was + 35.6 heat-units (Thomsen + 32.9 units).

The *heat of formation of cuprous iodide* was estimated by the action of potassium iodide on cupric sulphate or chloride in presence of hydrogen sulphite. The value deduced for $\frac{1}{2}\text{Cu}_2 + \frac{1}{2}\text{I}_2 = \frac{1}{2}(\text{Cu}_2\text{I}_2)$ was 16.9 units (Thomsen, 16.5). The observations of others on the necessity of using a reducing agent such as hydrogen sulphite in order to obtain pure cuprous iodide are confirmed. V. H. V.

Basic Salts; Atacamite. By BERTHELOT (*Compt. rend.*, **91**, 450—454).—The thermic relations of atacamite ($\text{CuCl}_2.3\text{CuO}.4\text{H}_2\text{O}$) and of the corresponding anhydrous oxychloride of copper are shown in the following reaction:—



Deducting these numbers from the heat of solution of $\text{CuCl}_2 + 11.0$, plus the heat evolved in the reaction $3\text{CuO} + 6\text{HCl} + 45.0$, it follows that—



The water being considered as solid, the last number becomes + 17.2 units.

Action of Dilute Potash on Atacamite.— $3\text{CuO}. \text{CuCl}_2.4\text{H}_2\text{O} + 2\text{KHO}$ (dilute), disengages + 0.34 heat-unit.

The reaction, $\text{CuCl}_2 + 2\text{KHO}$ (dilute), disengages + 27.4—15 = + 12.4 units; and since the heat of solution of CuCl_2 is + 11.0, we again get for the heat of formation of atacamite + 12.4—0.34 + 11.0 = + 23.0 units. It will be seen that the action of cupric chloride on cupric oxide and on potash disengages almost the same quantity of heat; so that very little energy is required to determine

* Kilogram-degrees.

the decomposition of potassium chloride by excess of cupric oxide. The heat of formation of anhydrous atacamite, $3\text{CuO} + \text{CuCl}_2$, is only +1.2 units. It is therefore to the presence of the 4 molecules of water that atacamite owes its stability. This explains the fact that a considerable temperature is required for the desiccation of this mineral, and that at this temperature the desiccated mass behaves almost exactly like a mixture of CuCl_2 with 3CuO .

The heat of formation of atacamite is so considerable, that it explains the observed production of this compound in a multitude of cases. Cupric oxide in excess should, for instance, be able to precipitate cupric chloride from its solution. In confirmation of this, the author has found that three equivalents of potassium hydrate in solution suffice to completely precipitate four equivalents of cupric chloride, leaving the filtrate neutral and colourless. The heat-units disengaged in acting on CuCl_2 successively with $\frac{1}{4}\text{KHO}$, $\frac{1}{2}\text{KHO}$, $\frac{3}{4}\text{KHO}$, and 1KHO are 2.24, 4.38, 6.0, and 6.2, nearly all the heat possible being disengaged by the action of $\frac{3}{4}\text{KHO}$. Since the heat of formation of $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$ is very nearly the same as that required for the decomposition of 3CuCl_2 by water into oxide and acid (at 100°), it is easy to conceive that atacamite has been formed by the action of heat or other disturbing influence on a solution of cupric chloride.

J. M. H. M.

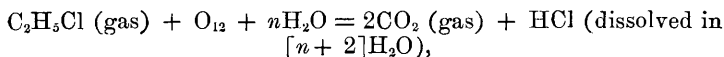
Thermochemistry. By BERTHELOT (*Compt. rend.*, **91**, 256—257).—In this note, the author calls attention to the agreement between the numbers published by him as the heat-units evolved in the combustion of carbonic oxide, marsh-gas, cyanogen, and hydrocyanic acid, and the corrected numbers recently found by J. Thomsen for the same substances. The true heat of formation of ammonia may now be considered as established.

J. M. H. M.

Contributions to the History of the Ethers. By BERTHELOT (*Compt. rend.*, **91**, 454—455).—The author has recently determined the heat of solution of methylic ether, and finds that at 17° $(\text{CH}_3)_2\text{O}$ dissolved in 200 parts H_2O , = +8.26 thermal units. Combining this result with data already known, it follows that $(\text{CH}_3)_2\text{O}$ (gas) + H_2O (gas) = $2\text{CH}_3\text{HO}$ (gas) corresponds with an *absorption* of 1.8 thermal units, and that $(\text{CH}_3)_2\text{O}$ (dissolved) + H_2O (liquid) = $2\text{CH}_3\text{HO}$ (dissolved) absorbs 0.1 thermal unit. This result is similar to that for ethylic ether.

$(\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O} = 2\text{C}_2\text{H}_5\text{HO}$ corresponds with absorption of 3.0 units (gases) and 0.5 unit (solutions).

The heat of combustion of ethyl chloride has been determined by burning ethyl chloride gas in presence of sufficient water to form a compound of definite thermal value with the resulting hydrochloric acid. The weight of $\text{C}_2\text{H}_5\text{Cl}$ burnt was determined (1) by the weight of HCl formed, and (2) by the weight of CO_2 formed. The mean result gave for the following reaction at constant volume:—



an evolution of 326.3 thermal units. Converting this to constant

pressure by adding 0.54 thermal unit, and deducting the heat of solution of the hydrochloric acid, the number +309.5 is obtained as the heat of combustion of C_2H_5Cl .

From this is deduced the heat of formation of C_2H_5Cl :—

C_2 (diamond) + H_2 + $Cl = C_2H_5Cl$ (gas) evolves + 348 — 309.5
= + 38.5 thermal units.

C_2H_5Cl (liquid) + 45.0 thermal units.

$C_2H_4 + HCl = C_2H_5Cl$ (gas) evolves + 341.4 — 309.5 = + 31.9
thermal units.

The heat of formation of amyl chloride (gas) deduced from the combination of amylene with hydrochloric acid, is little more than half the above number, viz., + 16.9 units. This difference of heat of formation of the primary and secondary chlorides corresponds with the unequal stability of the two compounds, and is analogous to the difference of heat of formation of ammonia salts of strong acids and of weak acids.

J. M. H. M.

Heat Phenomena of the Solution of Alcohols in Water and of Water in Alcohols. By W. ALEXEJEFF (*Bull. Soc. Chim.* [2], 34, 86—87).—Solution of butyl alcohol and fermentation amyl alcohol dissolved in water cause an evolution, the reverse action an absorption of heat. On addition of water to propyl alcohol in successive portions, at first there is an absorption, then an evolution of heat; the reverse action causes an evolution of heat. The observation of Bussy and Buignet (*Bull. Soc. Chim.* [2], 7, 160), that heat is absorbed when to a mixture of amyl alcohol and water in the portion corresponding to the hydrate, an excess of the alcohol is added has been verified by the author. These experiments show that for saturated alcohols there exist hydrates, the stability of which diminishes as the number of carbon-atoms in the molecule increases.

V. H. V.

Heat of Combustion of some Compounds of the Fatty Series. By W. LOUGUININE (*Compt. rend.*, 91, 297—300).—1. *Allyl alcohol*, $CH_2 : CH.CH_2(OH)$:—

C_3H_6O (liquid) + O_8 (gas) = $3CO_2$ (gas) + $3H_2O$ (liquid) =
442650.2 thermal units.

Acetone, $CO(CH_3)_2$, isomeric with the above, has, according to Favre and Silbermann, a calorific value of 423574 thermal units.

2. *Ethylvinylcarbinol*, $Et.C_2H_3 : CH(OH)$:—

$C_5H_{10}O$ (liquid) + O_{14} (gas) = $5CO_2$ (gas) + $5H_2O$ (liquid) =
753213.8 thermal units.

The difference of CH_2 in this series between this alcohol and the preceding, corresponds to a difference of 155281 heat-units; it must not be forgotten, however, that one is a primary and the other a secondary alcohol.

3. *Propylenic glycol (normal)*, $CH_2(OH).CH_2.CH_2(OH)$:—

$C_3H_8O_2$ (liquid) + O_8 (gas) = $3CO_2$ + $4H_2O$ (liquid) = 431170.8
thermal units.

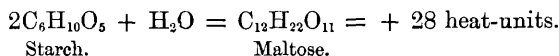
4. *Isopropylenic glycol*, $\text{CH}_2(\text{OH}).\text{CH}(\text{OH}).\text{CH}_3$, develops 436240.0 thermal units on combustion.

The difference between ethyl alcohol and ethylenic glycol is represented by 47171 heat-units, which corresponds closely with the difference between propyl alcohol (normal) and normal propylenic glycol, viz., 49142 heat-units. The difference between propyl alcohol and propylenic glycol (49142 heat-units) is greater than that between propylenic glycol and glycerol (38616 heat-units).

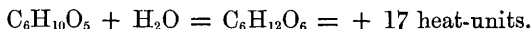
J. M. H. M.

Heat of Combustion of Carbon Compounds. By C. v. RECHENBERG (*J. pr. Chem.* [2], **22**, 223—250). (*Conclusion.*)—The greater part of this article is historical and not adapted for abstraction. The following are the results of the author's own investigations:—

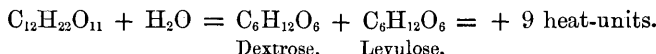
Action of diastase on starch below 65° :—



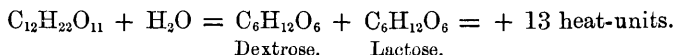
Action of dilute acids on starch:—



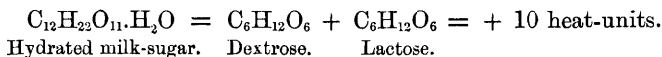
Action of dilute acids or inversion of cane-sugar:—



Action of dilute acids on milk-sugar:—



or—



Action of dilute acids on maltose on conversion into dextrose:—



or—

Maltose hydrate into dextrose hydrate:—



Inversion of cane-sugar in solution = + 6 units.

„ milk-sugar „ = + 9 „

Evolution of Heat during Alcoholic Fermentation.

I. Direct Fermentation.

Process.	Heat-units.	
	Heat of combustion of 1 mol. of compound.	Heat of combustion of 1 kilo. of compound.
Dextrose anhydride, $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$	+ 67	+ 372
„ $(HC_6H_{12}O_6)_2(gel.) = (2C_2H_5OH)_3(gel.) + 2CO_2$..	+ 74	+ 411
Dextrose hydrate, $C_6H_{12}O_6 \cdot H_2O = 2C_2H_5OH + 2CO_2 + H_2O$..	+ 59	+ 298
Lactose anhydride, $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$	+ 59	+ 328
Maltose anhydride, $C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2$	+ 140	+ 409
Maltose hydrate, $C_{12}H_{22}O_{11} \cdot H_2O = 4C_2H_5OH + 4CO_2$	+ 132	+ 367

II. Indirect.

Cane-sugar, $C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2$	+ 143	+ 418
„ $C_{12}H_{22}O_{11}(gel.) + H_2O = 4C_2H_5OH(gel.) + 4CO_2$..	+ 154	+ 450
Milk-sugar anhydride, $C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2$..	+ 139	+ 407
„ hydrate, $C_{12}H_{22}O_{11} \cdot H_2O = 4C_2H_5OH + 4CO_2$	+ 136	+ 378
„ $C_{12}H_{22}O_{11} \cdot H_2O(gel.) = 4C_2H_5OH(gel.) + 4CO_2$..	+ 149	+ 414
Starch, $C_6H_{16}O_5 + H_2O = 2C_2H_5OH + 2CO_2$	+ 84	+ 519
Cellulose, „ „ „	+ 79	+ 487
Metarabin, „ „ „	+ 81	+ 500
Inulin, „ „ „	+ 70	+ 432

Thermochemical Relation of Homologous and Isomeric Substances.

	Heat of combustion.	Difference.
Myristic acid, $C_{14}H_{28}O_2$	2175 units	} 4.158 units.
Stearic „ $C_{18}H_{36}O_2$	2808 „	
Oxalic „ $C_2H_2O_4$	59 „	} 148 „
Malonic „ $C_3H_4O_4$	207 „	
Succinic „ $C_4H_6O_4$	354 „	} 147 „
Benzoic „ $C_7H_6O_2$	811 „	
Phenyl-acetic acid, $C_8H_8O_2$..	969 „	} 158 „

	Melting point.	Heat of combustion.	Heat of formation.
Mannite	166°	760 units	287 units.
Dulcite	185.5	753 „	294 „
Salicylic acid.....	155—156	759 „	106 „
Metaoxybenzoic acid....	200	754 „	111 „
Paraoxybenzoic „	210	750 „	115 „

When naphthalene and anthracene are built up from their elements, heat is absorbed, amounting for the former to 42 units; for the latter 115 units.

The paper also contains proofs of the exactness of the author's method, with diagram of apparatus and comparisons with other methods.

G. T. A.

An Acoustic Method of Determining Vapour-densities. By H. GOLDSCHMIDT (*Ber.*, **13**, 768—771).—The author proposes to observe the notes produced on striking a test-glass filled with (α) the gas whose density is to be determined, and (β) atmospheric air. From these data the density can be calculated by the formula $d = \left(\frac{N}{n}\right)^2 = \left(\frac{\text{note in air}}{\text{note in gas}}\right)^2$, where N and n represent the number of vibrations of the two notes produced.

W. C. W.

Dilatation and Compressibility of Gases under High Pressures. By E. H. AMAGAT (*Compt. rend.*, **91**, 428—431).—The laws which the author has deduced from his researches on this subject are expressed as follows:—

1. The coefficient of dilatation of a gas (for temperatures not greatly above the critical temperature) increases with the pressure up to a maximum, beyond which it decreases indefinitely.

2. This maximum occurs at the pressure for which the product, $p\nu$, is a minimum, when the gas accidentally follows Marriott's law.

3. This maximum diminishes for temperatures more and more elevated, and ends by disappearing.

4. At a sufficiently high temperature the effect of pressure on fluids is represented by the formula $p(v - \alpha) = \text{constant}$, α being the smallest volume which the fluid can occupy. In each gas α has a special value.

5. For pressures below the critical pressure, the deviation, at first positive for a sufficiently low temperature, becomes *nil*, then negative as the temperature increases; but, after reaching a certain negative value, it diminishes indefinitely without change of sign.

6. For pressures between the critical pressure and a higher limit special for each gas, the period during which the deviation is positive is preceded, at a much lower temperature, by a period during which it is negative, so that the deviation changes sign twice.

7. Beyond the higher limit of pressure mentioned in the preceding law, the deviation is always negative, whatever the temperature may be; it generally diminishes as the temperature increases, except for pressures near the limit, when the variation is more complicated.

In a footnote, the value of α , referred to the unit of volume at 0° and normal pressure, is given for three gases: carbonic anhydride, 0.00170; ethylene, 0.00232; hydrogen, 0.00078.

In the first part of the paper, the author endeavours to explain the deviations from Marriott's law summed up in the above statements, by supposing the individual molecules of gas to be surrounded by an atmosphere of condensed ether.

J. M. H. M.

"Volume Constitution" of Liquids. By H. SCHROEDER (*Ber.*, 13, 1560—1571).—By comparing the volumes of liquids at their boiling points, it appears, first, that the volume of an acid is greater than that of the isomeric ethers; secondly, that the volume of a normal compound is greater than that of the secondary compound; thirdly, the boiling point and volume of such isomeric ethers as methyl acetate and ethyl formate, are greater in the case of the ether containing the acid radicle having the smaller molecular weight. Hence it appears that isomerides do not possess the same specific volume.

The difference between the boiling points of antimony bromide and chloride is less than that between the boiling points of phosphorus bromide and chloride, whereas the difference between the volumes of the former pair is greater than between those of the latter pair of compounds. The same phenomenon is exhibited by comparing analogous pairs of other compounds; for instance, isopentyl and isobutyl bromides with isopentyl and isobutyl chlorides; or isobutyl iodide and chloride with isopentyl iodide and chloride; or acetic and propionic acids with propionic and normal butyric acids; or the ethyl acetate and propionate with ethyl propionate and butyrate. It appears, therefore, that the difference in the boiling points of pairs of analogous compounds decreases with increase in molecular weight; whilst the differences of the volumes of such compounds increase with increase of molecular weight.

In the case of aldehydes and alcohols, the relationships are different. Thus the difference between the boiling points of methyl and ethyl alcohols is smaller than the difference between the boiling points of ethyl and propyl alcohols. The difference between the volumes is less in the case of the two first alcohols than in the case of the two last-mentioned alcohols.

It is evident that the differences between the volumes of corresponding compounds whose molecular weights differ by an equal amount, are not constant, but vary according to certain laws. Linne-man has shown that the differences between the boiling points vary in a similar manner.

The law of "steres," which the author regards as proved for solids, is also true for liquids. The volume of every component and every element of a compound may be expressed in simple multiples of the same mass or stere. Comparing volumes at the boiling points, it appears from the above that the stere increases with increase in molecular weight. In the case of aldehydes and alcohols, the opposite takes place. Further, it appears that the steres vary within narrow limits in the carbon compounds, the limits being 6·7 and 7·5. These numbers denote cubic centimeters when the molecular weights are expressed in grams.

The atoms of carbon, hydrogen, oxygen, and nitrogen in general occupy one stere, but the manner in which they are combined has some influence on the number of steres which an atom of these elements occupy.

An atom of oxygen united to two monovalent elements or radicles, occupies one stere, thus: methyl alcohol $C_1H_3O_1H_1 = 6 \times 7\cdot05 = 42\cdot3$, and ethyl alcohol, $C_2H_5O_1H_1 = 9 \times 6\cdot91 = 62\cdot2$.

An atom of oxygen united by two affinities to a carbon atom occupies 2 steres, *e.g.*, aldehyde, $C_1H_3C_1O_2H_1 = 8 \times \overline{7.10} = 56.8$, and propyl aldehyde, $C_2H_5C_1O_2H_1 = 11 \times \overline{6.82} = 75$. The specific volumes of acetic and propionic acids, calculated in the same manner, agree with those observed.

A double atom of hydrogen united with an atom of nitrogen occupies one stere; thus ammonia is $N_1H_3.H_1$; the amidogen group, NH_2 , occupies, therefore, 2 steres.

An atom of nitrogen combined with 1 atom of carbon, as in cyanogen, occupies 2 steres, as also when united by two bonds with an atom of oxygen or a double atom of oxygen.

A carbon atom united by three affinities to a nitrogen atom occupies 2 steres; so cyanogen is C_2N_2 , *e.g.*, methyl cyanide, $C_1H_3.C_1N_2 = 8 \times \overline{7.01} = 56.1$.

Two carbon atoms, united by two or more bonds, occupy a larger space; thus the volume constitution of allyl alcohol is $C_2H_5.C_1H_3O_1H_1 = 11 \times \overline{6.8} = 74.8$.

In the benzene compounds the 6 carbon atoms occupy 8 steres, and each hydrogen atom occupies 1 stere. Thus, benzene = $(C_6H_5)_1H_1 = 14 \times \overline{6.86} = 96$.

Phenyl, $(C_6H_5)_1^3$, has the same stere as isobutyl, C_4H_9 ; this is shown in the following case, *viz.*, phenol and isobutyl alcohol, benzyl alcohol, $(C_6H_5)_1^3.CH_2.OH$, and isoamyl alcohol, $C_4H_9.CH_2.OH$, and with benzaldehyde, $(C_6H_5)_1^3COH$, and isoamylaldehyde, $C_4H_9.COH$.

The monovalent elements, chlorine, bromine, and iodine, occur usually as Cl_2 , Br_2 , and I_2 : thus ethyl chloride, $C_2H_5Cl_2 = 10 \times \overline{7.07}$. Ethyl bromide, $C_2H_5Br_2 = 11 \times \overline{7.13}$, and ethyl iodide, $C_2H_5I_2 = 12 \times \overline{7.17}$.

A double atom of chlorine united with a single carbon atom, occupies 7 steres; thus carbon tetrachloride, $Cl_4C_1 = 15 \times \overline{6.96}$, chloroform, $H_1Cl_3C_1Cl_2 = 12 \times \overline{7.04}$; chloral, $C_1Cl_3C_1^3.C_1O_1H_1 = 15 \times \overline{7.11}$.

An atom of sulphur, united with monovalent elements or radicles, occupies 3 steres; *e.g.*, methyl thiocyanide, $C_1H_3S_1C_1N_2 = 11 \times \overline{7.11}$; and ethyl sulphide, $C_2H_5.S_1C_2H_5 = 17 \times \overline{7.15}$.

When an atom of sulphur is united by two affinities to a polyvalent element, then it occupies 4 steres; thus, $S_1^2C_1S_1^2 = 9 \times \overline{6.92}$.

The specific volumes of the above compounds, as calculated, agree tolerably well with the experimental determinations of one or more of the observers, Kopp, Pierre, and Thorpe.

Finally, the author shows that volume constitution of bodies is the same in the liquid and solid states. Thus solid iodine is $I_2 = 5 \times 5.14$; chlorine is Cl_2 in its solid and liquid compounds; and bromine is Br_2 under similar conditions.

Rhombic sulphur is $S_8 = 3 \times \overline{5.2}$; monoclinic sulphur, $S_8 = 3 \times \overline{5.4}$; and plastic sulphur is $S_8 = 3 \times \overline{5.53}$, and in its fluid compounds it is also S_8 .

Cyanogen in solids and liquid compounds occupies 4 steres. Nitro-

gen in nitric acid and nitrates occupies 2 steres. A double atom of hydrogen combined with 1 atom of nitrogen has 1 stere in compounds in the solid and liquid state.

This agreement is further exhibited by solid and liquid formic and acetic acids, also by the silver salts of the fatty acids and by those of their salts with alcohol radicles which are liquid. P. P. B.

Relations between the Physical Properties of Carbon Compounds and their Chemical Constitution. By J. W. BRÜHL (*Ber.*, 13, 1520—1535).—From a consideration of the results of his investigations of the refractive powers of liquid organic compounds, the author draws the following conclusions:—

First, the specific and molecular refractive powers of isomeric saturated compounds are identical. This conclusion is supported by the equality of the refractive power in the following instances, viz., ethylene and ethylidene dichlorides; propyl and isopropyl alcohols, bromides, and iodides; butyl and isobutyl iodides; and finally normal butyl, secondary, and tertiary butyl alcohols.

It is evident, therefore, that the grouping of the atoms in saturated compounds has no influence upon the specific or molecular refractive powers of isomerides.

Secondly, in the case of isomerides of unsaturated compounds, which contain the same number and species united by two bonds, the specific refractive powers of such isomerides are identical. This is shown to be the case in the following pairs of isomerides, all of which contain an atom of oxygen joined by two affinities to one carbon atom, and possessing the atomic refractive power 3·4, viz., in propyl aldehyde and acetone, butyl and isobutyl aldehydes, butyric and isobutyric acids, butyric and isobutyric chlorides.

The molecular refractive power of a compound indicates whether any of the atoms are united with one another by two affinities, and also the number of such cases; it further gives a clue as to which atoms are so united. This statement is illustrated by the isomerides allyl alcohol, acetone, and propylene oxide, the molecular refractive powers of which are different. In the first, there are two carbon atoms united by two bonds; in the second, the oxygen atom is united by two bonds to one carbon atom; and in the third, the oxygen atom is united by single bonds to two different carbon atoms.

In the case of two isomerides having the refractive indices n and n_1 , and densities d and d_1 , then if the isomerism be due to a difference in the degree of saturation of the valencies of the atoms, then $n - 1 : d > n_1 - 1 : d_1$, and therefore the refractive indices minus one, or the “refractive powers,” are not proportional to the densities of the isomerides.

If, however, the isomerism arises from the difference of the groups of atoms in the molecule, then from the above it follows that $\frac{n-1}{d}$ = $\frac{n_1-1}{d_1}$, and hence $n - 1 : n_1 - 1 :: d : d_1$, or the “refractive

powers" are proportional to the densities. From this the author was led to the examination of the densities of such isomerides. The densities of the following, viz., ethylene and ethylidene dichlorides, some propyl and isopropyl compounds, and some butyl and isobutyl compounds, show that the density of the normal is greater than that of its secondary isomeride. The refractive indices of such isomerides vary in the same manner as their densities, and a similar relationship has been shown to hold for the boiling points of normal and secondary compounds.

The determinations of the times of transpiration of molecular quantities of propyl and isopropyl alcohols, of butyric and isobutyric acids, and of benzyl chloride and chlorotoluene, show that the times of transpirations of molecular quantities of normal and secondary compounds are related in a manner similar to the alteration in their densities, refractive indices, and boiling points.

The times of transpiration of molecular quantities of the fatty acids are greater than those of the isomeric alcoholic salts, *e.g.*, the time of transpiration of propionic acid is greater than that of ethyl formate or of methyl acetate. The boiling points, densities, and refractive indices of the acids are also greater than those of the isomeric salts. These constituents are in the case of alcohols greater than those of the isomeric ethers, *e.g.*, in case of butyl alcohol and ethyl ether.

It therefore appears probable that the specific viscosities, boiling points, densities, and refractive indices of liquid carbon compounds are all related to their chemical constitution, and that all these constants are greater in the case of the normal compound than in the case of the isomeric secondary one.

That the specific volumes of liquid carbon compounds are influenced by the manner in which the atoms are united, has been shown by various authors (Thorpe, this Journ., Trans., 1880, 370). The author shows that in the case of the isomerides, ethylene and ethylidene dichlorides, the molecular density is greater, or the specific volume is less, in the case of the isomeride whose boiling point, specific gravity, refractive index, and times of transpiration are greater. P. P. B.

Stability of Hydrogen Peroxide. By BERTHELOT (*Bull. Soc. Chim.* [2], 34, 78—80).—The spontaneous decomposition of hydrogen peroxide into water and oxygen is in accordance with thermochemical theory. The author has made a few experiments on the rate of the change. For the first month, the decomposition of a solution containing 3.85 O (corresponding to 8.18 H_2O_2) in the litre, and 0.15 gram H_2SO_4 at a temperature of 10—15° C., can be expressed by the formula $T = 0.094t + 3.85$. At the end of the month, the rate of decomposition slackens gradually, but the change is not complete even at the end of two years. Solutions acidified with hydrochloric acid decompose more slowly. The stability of the solutions does not depend on its "acid titre," but on the absence of every trace of any base or free alkali. Concentrated solutions decompose far more rapidly than those which are dilute. The curve of change for the first period of time is coincident with its tangent; as the reaction diminishes, it is an asymptote. Exactly similar phenomena take place

in the spontaneous decomposition of ozone. The author makes some remarks on the stability of compounds under the influence of dilution.

V. H. V.

Decomposition of Salts by Liquids. By A. DITTE (*Compt. rend.*, **91**, 576—579).—The laws of the decomposition of salts by liquids are analogous to those which govern the dissociation of bodies by heat. For example, calcium oxychloride is obtained by the action of milk of lime on a hot concentrated solution of calcium chloride, the salt being deposited in crystals as the liquid cools. On gradually adding these crystals to water, they are decomposed into calcium chloride and calcium hydrate, until a point is reached when the liquid contains (at 10°) 85 grams per litre of calcium chloride in solution. Beyond this, the oxychloride when added, dissolves without decomposition. Hence milk of lime added to a solution containing less than 85 grams of calcium chloride per litre will have no action; but if added to a solution containing more, the excess will be converted into calcium oxychloride. The same laws were found to govern solutions of calcium chloride in various alcohols, but with of course different proportions of the quantities according to the temperature and the nature of the alcohol.

R. R.

Chemical Affinity. By W. OSTWALD (*J. pr. Chem.* [2], **22**, 251—260).—Second paper—(Compare this Journal, Abstr. 1879, p. 348).—The first point which the author endeavours to settle is whether during the mutual reaction of solid and liquid bodies on each other, a permanent state of equilibrium can be reached. The experiments were made chiefly by acting on calcium oxalate with free acids, and calculating the results by titration with potassium permanganate.

When calcium oxalate (however prepared) is brought into contact with an acid, a certain part is dissolved, and the quantity remains unaltered, no matter how long the mixture of the acid and the salt is left standing, provided that the temperature remains unchanged. The quantity of oxalate, if it is only in excess, has no influence whatever on the part dissolved. The state of equilibrium seems to be reached at once in this case, but it is not so with other salts—barium chromate, for instance, requires weeks or months before it reaches a state of equilibrium with the acid used.

The next question is whether this state of equilibrium is independent of the original arrangement of the substances, and the experiments seem to show that it is. Taking equivalent quantities of lime, hydrochloric acid, and oxalic acid, the lime may be combined with the oxalic acid, and the calcium oxalate decomposed by hydrochloric acid, or a solution of calcium chloride may be mixed with oxalic acid. The first case has already been described: in the second case, there is at first excess of oxalic acid in the solution; but after shaking the mixture up and allowing it to stand for four to six weeks, a state of equilibrium is reached, which is identical with the result obtained in the first case.

The same quantity of calcium oxalate finally remains in solution in hydrochloric acid, even when a larger quantity has been at first dissolved either by raising the temperature or by dehydrating the salt.

The salt containing 1 mol. H_2O seems to be the most stable of the calcium oxalates, so that the dehydrated oxalate, as well as the one containing 3 mols. H_2O , are both finally converted into it. Zinc oxalate shows a similar deportment. When chromic acid and chloride of barium are mixed together, the state of equilibrium is reached sooner in dilute than in concentrated solutions.

G. T. A.

Lecture Experiments. By V. MERZ and W. WEITH (*Ber.*, **13**, 718—724).—I. Dry carbonic oxide is absorbed by soda lime at 200° , with formation of sodium formate; if moist carbonic oxide is employed, hydrogen is evolved, the formate being decomposed by the soda into carbonate and hydrogen.

II. The conversion of formic into oxalic acid is easily shown by heating about 2 grams of sodium formate in a test-tube, until the fused mass begins to solidify. The residue dissolved in water is precipitated by calcium chloride in presence of acetic acid.

III. If chloride of calcium is dropped into a flask containing potassium iodide in a state of fusion, the vapour of iodine is at once apparent. The decomposition does not take place if the air in the flask is replaced by carbonic anhydride.

IV. Pure sulphuretted hydrogen has no action on metallic copper or silver, unless air is present. If copper (precipitated from a solution of the sulphate by metallic zinc) is brought into a cylinder containing 2 vols. of oxygen and 1 of sulphuretted hydrogen, it immediately turns black, then grows red hot and ignites the sulphuretted hydrogen.

V. When a piece of cold porcelain is held in a phosphoretted hydrogen flame, phosphorus is deposited.

W. C. W.

Inorganic Chemistry.

Preparation of Hydrogen Selenide and Hydrobromic Acid.

By A. ETARD and H. MOISSAN (*Bull. Soc. Chim.* [2], **34**, 69).—The authors prepare hydrogen selenide by a method analogous to that employed by Champion and Pellet for hydrobromic acid and hydrogen sulphide, that is, by the action of bromine and sulphur respectively on paraffin. The hydrocarbon used in preparing hydrogen sulphide was colophene, as its boiling point (300°C.) is considerably above the fusing point of selenium (250°C.). The reaction takes place in two stages: at first a substituted product is formed, and this is subsequently decomposed; at the end of the experiment nothing but a mixture of unaltered colophene and carbon is left. Hydriodic acid may be prepared by a similar process. V. H. V.

Liquefaction of Ozone, and its Colour in the Gaseous State.

By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **91**, 522—525).—The authors obtained a mixture very rich in ozone by the action of electricity on oxygen at a very low temperature. This mixture was transferred to the capillary tube of Cailletet's apparatus, and sub-

mitted to pressure, at a temperature of -23° . At the first few strokes of the piston an azure-blue colour was seen to fill the tube and as the pressure increased the colour deepened, until when the gas was under a pressure of several atmospheres, the colour had become indigo-blue. When the pressure was suddenly removed, a momentary white mist was observed within the tube, indicating a condensation into the liquid, or perhaps solid state. The blue colour, being like its odour, an essential property of ozone, may be seen whenever a sufficient thickness of a mixture containing it is viewed. Thus the oxygen issuing from Berthelot's silent-discharge apparatus exhibits a sky-blue colour when viewed along a column 1 metre in length. In a forthcoming communication, the author will discuss the agency of ozone as affecting the colour of the atmosphere. R. R.

Constancy of the Proportion of Carbonic Anhydride in the Atmosphere. By T. SCHLOESING (*Compt. rend.*, 90, 1410—1413).—The author is of opinion that the sea plays an important part in regulating the quantity of carbonic anhydride present in the atmosphere. He has shown (*ibid.*, June and July, 1872) that water in contact with the carbonate of an alkaline earth, and an atmosphere containing carbonic anhydride, absorbs the latter, forming a quantity of bicarbonate, which increases with the tension of the carbonic anhydride in the atmosphere, according to a given law. Moreover, if the water contains a neutral salt, the amount of bicarbonate formed is increased. Comparing this with the state of the sea and the atmosphere, it is seen that the sea is in constant contact with air which contains carbonic anhydride, and with the earthy carbonates at its bottom. From analyses of sea water, the author finds that 1 litre contains 98.3 mgrms. of carbonic anhydride, and a base combined with it equivalent to 99.3 mgrms. sulphuric acid, so that the greater part exists in the form of bicarbonate. Now when the amount of carbonic anhydride in the atmosphere, which is proportionately very much less than that contained in sea water, increases beyond its normal amount, the surplus is absorbed by the sea and a fresh portion of the earthy carbonates goes into solution. On the other hand, when the quantity decreases, carbonic anhydride escapes into the atmosphere. This action, together with the continual motion of the atmosphere, tends greatly to equalise the quantity of the gas present in the atmosphere. L. T. O'S.

Proportion of Carbonic Anhydride in the Atmosphere. By J. REISET (*Compt. rend.*, 90, 1457—1459).—This is a reply to Marie-Davy, in which the author maintains that the method of experiment used by the observer at Montsouris to determine the constancy of the proportion of carbonic anhydride in the air was not sufficiently exact to eliminate all sources of error: also that the experiments of Truchot on the influence of altitude on the amount of carbonic anhydride require repetition, since no correction is made for the alteration in the standard solutions due to evaporation at such high altitudes. The author quotes his former remarks (*this Journal*, Abstr., 1880, 605). L. T. O'S.

Proofs of the Existence of Ozone in the Atmosphere. By E. SCHÖNE (*Ber.*, **13**, 1503—1508).—Hydrogen peroxide has been shown by the author (this Journal, **34**, 552 and 703) to be a constituent of the atmosphere. This being the case, the evidence adduced by Schönbein and Houzeau to prove the existence of ozone in the atmosphere is of little value, for the results they obtained may have been produced by hydrogen peroxide. Little weight is to be attached to the evidence brought forward by Andrews (*Phil. Mag.* [4], **34**, 315; and *Nature*, **8**, 347 and 364); or Fox ("Ozone and Antozone," London, 1873, 48 and 216), in support of the existence of ozone in the atmosphere, these authors having ignored the presence of hydrogen peroxide completely. The method of testing for ozone by exposing silver foil is one to which many objections may be raised. The odour observed after a flash of lightning and attributed by many to ozone, the author fails to recognise as resembling that of ozone.

The author concludes that the evidence in favour of the existence of ozone in the atmosphere is by no means conclusive, yet in atmospheric electricity we have power sufficient for its production. The existence of hydrogen peroxide in the atmosphere does not exclude that of ozone, since these bodies decompose one another but slowly.

P. P. B.

Observations on the Atmosphere made with Thallium Papers. By E. SCHÖNE (*Ber.*, **13**, 1508—1514).—The observations of the author and others show that the ozonometer of Schönbein (*Annalen*, **89**, 226), is too much influenced by the hygroscopic state of the atmosphere to be of service in determining the combined effect of ozone and hydrogen peroxide present in the atmosphere. This ozonometer the author stigmatises as a crude hygrometer. As the oxidation of thallous hydrate by ozone or hydrogen peroxide is uninfluenced by the presence of moisture, the author has made a series of daily and nightly observations by exposing to the atmosphere papers saturated with a 2 per cent. solution of thallous hydrate. A scale of numbers was made corresponding with the densities of the brown colour produced by exposure. Observations were made simultaneously with the ozonometer, the deductions from which were usually the opposite of those obtained from the thallous hydrate. The observations with thallous hydrate show that the oxidation is greater during the day than during the night; it is influenced by the direction of the wind, a southerly wind is attended with a stronger coloration; clouds and rain have a marked influence, viz., the reduction of the coloration of the thallium paper. Further allowance must be made for the strength of the wind. The observations made with thallium papers agree with the results obtained by the author in the more exact determination of the atmospheric hydrogen peroxide. From this fact, the author thinks that atmospheric hydrogen peroxide is sufficient to produce the observed oxidation, and that the presence of atmospheric ozone is uncertain.

P. P. B.

Position of Boron in the Series of Elementary Bodies. By A. ETARD (*Compt. rend.*, **91**, 627—629).—The author proposes to place boron at the head of the vanadium family of elements, forming

a group intermediate between that of phosphorus and that of carbon. This juxtaposition of boron to the phosphorus group is supported by the existence of the compounds BCl_3 and BOCl_3 , recently discovered by Counceler, and by the existence of boric triethide or triethylborine, which is analogous to triethylphosphine in composition and properties. The relations of vanadium to the phosphorus group have been established by Roscoe, and the labours of Deville and Troost have done as much for niobium and tantalum. Boron and vanadium are both grey, pulverulent, carbon-like substances, combustible, and infusible; both combine with chlorine, forming BCl_3 and VCl_3 , and their oxychlorides, BOCl_3 and VOCl_3 , are yellow fuming liquids. Boron and vanadium, like the other members of the group, B, V, Nb, Ta, have also the somewhat rare property of directly absorbing nitrogen. The author will, in a subsequent communication, describe the properties of an oxide of boron, B_2O_5 , corresponding with V_2O_5 and P_2O_5 .

R. R.

Action of Sulphur on Water. By A. COLSON (*Bull. Soc. Chim.* [2], 34, 66—69).—The author was induced to study the action of sulphur in the nascent state on boiling water, from difficulties which arise in the determination of iron by the Marguerite process. On adding a very dilute solution of sodium thiosulphate to dilute hydrochloric acid (1 : 10), the salt is completely decomposed, with formation of hydrogen sulphide and sulphuric acid, the reaction being $\text{S}_2\text{O}_2 + \text{H}_2\text{O} = \text{SO}_3 + \text{H}_2\text{S}$. In more concentrated solutions the decomposition is not so complete, part of the sulphur being deposited on the sides of the flask. An experiment with sulphur dissolved in sodium protosulphide showed that an amount of lead sulphide was obtained greater than that required by theory for the protosulphide employed. A comparison is drawn between the action of water on flowers of sulphur and on sulphur liberated from the thiosulphate. The latter is energetic, and takes place at once at ordinary temperatures; the former requires time, and the temperature of boiling water. The sulphur deposited on the flask from the decomposition of the strong thiosulphate solution, was in the form of lemon-yellow grains, which had no action on polarised light. The same form was obtained from sulphur deposited from a benzene solution, and kept for some time in contact with boiling water. It would appear that sulphur loses its crystalline form before entering into combination.

V. H. V.

Presence of Cerium in the Coal Measures of St. Etienne. By MAYENCON (*Compt. rend.*, 91, 669).—The paper notes the author's discovery of cerium in some mineralogical products of the mining district of St. Etienne. The cerium is found particularly in certain hard nodules of carbonate of iron, where it appears to exist in the state of carbonate.

R. R.

Sesquioxide of Chromium. By H. MOISSAN (*Bull. Soc. Chim.* [2], 34, 70—73).—The author compares the action of various reagents on ignited chromium sesquioxide and the oxide rendered anhydrous by heating it at 440°C . in a current of nitrogen or carbonic anhydride. Hydrogen sulphide and selenide, chlorine, bromine, and

oxygen have no action on the former modification. The actions of some of these substances on the other modification are studied.

Action of Hydrogen Sulphide.—By exposing the anhydrous oxide to a current of hydrogen sulphide, whether dry or moist, at 140°C. , it is converted into the corresponding black sulphide, Cr_2S_3 . The substance is not attacked by any acid except nitric acid and aqua regia. By reducing it in hydrogen, a black protosulphide, CrS , is formed.

Action of Oxygen.—The sesquioxide when heated in this gas is converted into the dark grey dioxide, CrO_2 , which resembles the corresponding manganese dioxide, MnO_2 , in its reactions.

Action of Chlorine.—By exposing the hydrated sesquioxide to a current of dry chlorine and gradually raising the temperature, red vapours of chlorochromic acid begin to be evolved at 440°C. , but with the anhydrous sesquioxide, dry chlorine forms the sesquichloride, the reaction being very incomplete: moist chlorine gives chlorochromic acid with the anhydrous sesquioxide or sesquichloride. It would appear from these experiments that the presence of small quantities of water determine the formation of chlorochromic acid, the necessary oxygen being furnished by the water. By stopping the reaction at a certain stage, the sesquioxide is converted into the brown oxychloride of Moberg, an intermediate body less oxidised than chlorochromic acid, and decomposable by water. The sesquioxide of chromium is a type of those oxides in which a change of properties is accompanied by an evolution of heat.

V. H. V.

Preparation of Chlorine. By BERTHELOT (*Compt. rend.*, **91**, 252—256).—The author's experiments were undertaken to elucidate the first stage of the reaction which occurs in the preparation of chlorine by the action of hydrochloric acid on manganese dioxide. When these substances are mixed in the cold, a brown liquid is formed, which was supposed by Forchhammer to contain a sesquichloride of manganese, by Nicklès and by Fisher (this Journal, **3**, 409) to contain manganese tetrachloride.

Action of Chlorine on Manganous Chloride.—A concentrated solution of manganous chloride, saturated with chlorine, and placed in contact with an atmosphere of this gas, dissolves only about half the quantity dissolved under the same circumstances by pure water, and about the same amount of heat is evolved in proportion to the chlorine dissolved in the two cases. The liquid slowly deposits a precipitate of manganese dioxide, absorbing at the same time an additional quantity of chlorine, but even after two months the ratio of chlorine absorbed to manganous chloride taken did not exceed 1 : 55. By diluting the original solution of manganous chloride saturated with chlorine with nine times its volume of water, an abundant precipitate of manganese dioxide is formed at once, which increases during a certain time. At the end of two months, the liquid still contained manganous chloride and free chlorine, coexisting with the hydrochloric acid and manganese dioxide formed: there is in fact an equilibrium established.

Action of Hydrochloric Acid on Manganese Dioxide.—Manganese dioxide mixed with a nearly equivalent quantity of a dilute (10 c.c. = 0.16 gram) solution of hydrochloric acid, evolves chlorine, and a

brown liquid is formed, but the reaction is very incomplete. If the same mixture be heated in a sealed tube at 100° for 20 hours, the reaction proceeds further, but remains incomplete. After cooling, manganese dioxide slowly separates out on the wall of the tube, proving that the equilibrium is dependent on the temperature.

Action of Chlorine on Manganous Chloride and Hydrochloric Acid.—On passing a current of chlorine into a concentrated solution of manganous chloride mixed with its own volume of strong hydrochloric acid, the liquid turns brown almost immediately, but deposits no precipitate even after three months. If the preceding solution be diluted ten times before saturating with chlorine, it absorbs about the same quantity of that gas without any coloration or precipitate being at first produced, but after some weeks a small quantity of manganese dioxide separates out on the walls of the flask. The heat evolved during the absorption of chlorine by manganous chloride in presence of hydrochloric acid is several times as great as that evolved in the absence of hydrochloric acid.

The author concludes from these experiments that the brown colour is due to the formation of a compound perchloride, which may be considered as $\text{HCl}.\text{Cl}_2 + n\text{MnCl}_2$, or as $n\text{HCl} + \text{MnCl}_4$. On the first view, this perchloride is derived from the perchloride of hydrogen, $\text{HCl}.\text{Cl}_2$, described by the author in a previous paper. This compound dissociates under the influence of heat, and the dissociation is rendered complete when the chlorine is removed as fast as it is liberated. When the experiment is conducted in sealed tubes, reabsorption of the chlorine takes place on cooling, attended with separation of manganese dioxide. The influence of dilution is twofold; in the first place the manganous chloride is partly decomposed by the water into oxide and free acid, and the oxide is peroxidised by the combined action of the free chlorine and water; in the second place, absorption of energy takes place by the formation of definite hydrates of hydrochloric acid, and in consequence of this loss of energy, the manganous chloride may be partly transformed into dioxide even in presence of hydrochloric acid, the equation MnCl_2 (dilute) + $2\text{H}_2\text{O} + \text{Cl}_2$ (gas) = $\text{MnO}_2 + 4\text{HCl}$ (dilute) corresponding with a disengagement of 3.7 thermal units. This reaction is never complete, on account of the secondary formation of $\text{HCl}_3 + n\text{MnCl}_2$.

The equation $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2$ (anhydrous) + 2Cl (gas) + $2\text{H}_2\text{O}$ (gas), corresponds with a disengagement of 12.9 thermal units, and this takes place to a greater or less extent in concentrated solutions, in which a portion of the hydrochloric acid is not combined with the water as a stable hydrate, the heat of formation of which is from 10 to 12 thermal units.

J. M. H. M.

Borodecitungstic Acid and its Sodium Salts. By D. KLEIN (*Compt. rend.*, 91, 474—475).—When a solution containing borax and boric acid in the proportion of 1 mol. of the former to 2 mols. of the latter is heated with an excess of tungstic acid (hydrated), a portion of the latter is dissolved. On cooling the filtered solution deposits crystals of boric acid and polyborates of sodium, and by continuing the evaporation of the mother-liquor *in vacuo* crystals of borax

are first obtained, and then a salt excessively soluble in water, and very difficult to purify by recrystallisation. This salt has the composition $2\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O} \cdot 10\text{WO}_3 \cdot \text{B}_2\text{O}_3 + 11\text{Aq}$. The crystals belong to the clinorhombic system, but are ill-defined, with dull faces. The reaction is faintly acid to litmus. On adding a trace of alkali, the acid reaction is changed to alkaline, but reappears after a time. By adding as much soda as is already present, and evaporating, a second crystalline salt is obtained, which has not yet been analysed.

Sodium borodecitungstate is precipitated by salts of mercury, and from this precipitate the acid may be obtained. This acid and boroduodecitungstic acid correspond with the silicodecitungstic and silicoduodecitungstic acids described by Marignac, and their salts have very similar properties.

J. M. H. M.

Boroduodecitungstic Acid. By D. KLEIN (*Compt. rend.*, **91**, 495—498).—When tungstic hydrate in large excess is added to a boiling solution of potassium pentametaborate, potassium boroduodecitungstate is formed. The author ascribes to this compound the formula $2\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 2\text{H}_2\text{O} + 15\text{Aq}$. It is a very soluble salt, crystallising in needles resembling those of potassic tungstoborate. The mother-liquor yields white tabular crystals of another salt, of the formula $4\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 12\text{WO}_3 + 21\text{Aq}$. By treating the insoluble mercurous salt with the requisite quantity of hydrochloric acid, and evaporating the solution after removal of the mercurous chloride, boroduodecitungstic acid is obtained as a syrupy liquid.

R. R.

Mineralogical Chemistry.

The Zündererz or Tinder-ore of Clausthal. By B. RÖSING (*Jahrb. f. Min.*, 1879, 157).—An analysis of this mineral gave the following results:—

Pb.	Cu.	Ag.	Fl.	Sb.	S.	
33·41	0·58	0·05	1·66	36·81	27·49	= 100·00

From this analysis, the formula appears to be $\text{Pb}_4\text{Sb}_6\text{S}_{17}$, and the mineral an impure bournonite (bleispiessglanz), in which a part of the lead has been replaced by copper, silver, and iron. The author is of opinion that zündererz is the final product of the decomposition of an antimonial galena. C. A. B.

Freislebenite from Hiendelaencina, Spain. By H. BÜCKING (*Jahrb. f. Min.*, 1879, 161).—Some of the crystals of this mineral attain a size of 6 mm. Two new twin-laws were observed occurring on the crystals from this locality, twins according to the well-known law, “the twin-plane $\infty P \infty$ ” not having been observed. In consequence of repeated combination, the crystals exhibited the characteristic

striation parallel to the zonal axes of the prisms and clinodromes. The two new twin-laws are as follows, viz. :—(1.) The twin-plane, a hemipyramid, probably ∞P_4 ; the prisms observed were ∞P_2 and ∞P , whilst the domes were $\frac{3}{2}P_\infty$ and $\frac{1}{2}P_\infty$. (2.) The twin-plane, a face of a prism, probably ∞P_5^6 . The same forms as those observed in No. 1 occur also in combination in this case. In addition, the following forms were observed, occupying a very secondary position, viz., ∞P_5 , ∞P_3 , ∞P_4^5 , $\frac{5}{4}P_\infty$, and $\frac{3}{4}P_\infty$. Thirty forms have now been observed on freislebenite.

C. A. B.

Quartz from the Eleanore Mine, on the Dünstberge, near Giessen. By A. STRENG (*Jahrb. f. Min.*, 1879, 156).—The quartz in question occurs in isolated broken crystals or in druses, enclosed in brown iron ore, the forms observed by him being R.—R. ∞P , and a prism having probably the symbol $\infty P_{\frac{1}{7}}$. The terminal edges of R. were modified by a semi-scalenohedron, but its faces were so small that no measurements could be made. The quartz from the Eleanore Mine resembles closely that from Striegau, described by Websky (*Jahrb. f. Min.*, 1871, 732).

C. A. B.

Fluid Enclosures in Topaz. By T. ERHARD and A. STELZNER (*Jahrb. f. Min.*, 1879, 158—159).—According to Vogelsang, the very expansive fluid which occurs in quartz, topaz, and other minerals is liquid carbonic acid, its “critical point” being 30° to 32° C. The authors conducted a very careful series of experiments, using a microscope which was kept at the same temperature as the object by means of a water-bath. Two topaz crystals were examined, containing in all seven fluid enclosures. Each fluid enclosure contained two other enclosures. The results of the investigation were briefly as follows, viz. :—1. For one and the same enclosure the globule disappeared and reappeared with intumescence at the same temperature. 2. The “critical points” of the fluid enclosures in different specimens are not quite identical. 3. As the “critical points” were found to lie between 28.745° and 29.18° C. the authors concluded that the fluid enclosures could not be pure carbonic acid, as the “critical point” of that substance is about 30.92° C.

C. A. B.

Andalusite from Brazil. By E. BERTRAND (*Jahrb. f. Min.*, 1879, 161—162).—The author examined some rounded crystals from Brazil which were partly light coloured and partly opaque, and strongly dichroitic. They scratched quartz. Sp. gr. = 3.16 to 3.20 .

C. A. B.

Artificial Analcime. By A. DE SCHULTEN (*Compt. rend.*, 90, 1493—1495).—On heating a solution of sodium silicate or caustic soda at 180 — 190° with an alumina glass for about 18 hours, small crystals covered with a lamellar layer of gelatinous silica are found adhering to the sides of the tube. These, when examined microscopically, appear transparent, of the form of a trapezohedron of the first system. Hydrochloric acid acts but slowly on them. The analysis shows that the crystals are a silicate of sodium, aluminium, and cal-

cium, of the same composition as natural analcime. Their action on polarised light has been studied. L. T. O'S.

A New Occurrence of Gismondine. By L. ROTH (*Jahrb. f. Min.*, 1879, 157).—Crystals of this mineral occur in drusy cavities, accompanied by crystals of chabasite and phillipsite, in the basalt of the Vogelsgebirge, between Gedern and Oberseemen. They are identical with those found at Schiffenberg and Burkhardt. The crystals are rhombic pyramids, 2 to 8 mm. in size, partly simple, partly penetration twins, similar to those from Schiffenberg, described by Streng (*Jahrb. f. Min.*, 1874, 578). They are also often coated with a yellow crust or with hyalite, but there is always a clear kernel.

C. A. B.

Occurrence of Prehnite in Tuscany. By A. CORSI (*Jahrb. f. Min.*, 1879, 161).—This mineral occurs—1. At *Impruneta*, in gabbro, of which it is a “decomposition-product.” The crystals are sometimes tabular, exhibiting the forms $OP.\infty P\infty.\infty P\infty.\infty P$ in combination (OP being strongly striated), and sometimes colourless aggregates of crystals. The prehnite is occasionally accompanied by analcime, which decomposes into prehnite. 2. At *Figline* in tabular crystals, not exhibiting many forms, and accompanied by albite and acicular zeolites. 3. At *Montecatini*, in the Cecina valley, in hollow spaces in gabbro; prismatic crystals are found exhibiting the forms $\infty P.\infty P\infty.OP$ in combination, and accompanied by calcite and native copper. 4. At *Monte Perrone*, on Elba, tabular crystals and crystal-line aggregates, in diorite, accompanied by epidote.

C. A. B.

Acmite and Aegerine. By C. DÖLTER (*Jahrb. f. Min.*, 1879, 157—158).—In the present paper the author continues his researches into the composition of these minerals, the previous results being published in the *Jahrb. f. Min.* 1878, 657.

Aegerine from Brevig.—Sp. gr. 3.501. Chemical composition as follows, viz. :—

SiO ₂ .	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.
51.74	26.17	3.48	0.47	0.46	5.07	1.79	0.34	11.02 = 100.54

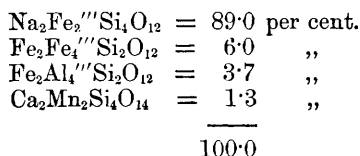
This analysis agrees with those already published. The small quantity of potash found is the constituent of orthoclase, which is present in microscopical particles in the aegerine. Dölter considers the constitution of aegerine to be as follows, viz. :—

$Na_2Fe_2'''Si_4O_{12}$	=	77.0	per cent.
$Ca_2Mg_2Si_4O_{12}$	=	9.9	„
$Ca_2Fe_2Si_4O_{12}$	=	11.6	„
$Ca_2Mn_2Si_4O_{12}$	=	1.5	„
<hr/>			
100.0			

Acmite.—This mineral is crystallographically identical with aegerine. Sp. gr. 3.520. Chemical composition as follows, viz. :—

SiO ₂ .	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.
51.35	32.11	2.59	1.59	0.37	—	—	—	11.39

Acmite is generally weathered, but the author selected fresh specimens for analysis. He found a smaller intermixture of other silicates in this mineral than was the case in aegerine. The constitution of acmite, according to Dölter, is as follows, viz.:—



From the above it would appear that a silicate having the formula $\text{Na}_2\text{Fe}_2''' \text{Si}_4\text{O}_{12}$ must be present in acmite and aegerine.

C. A. B.

Dolomite of South Tyrol. By H. LORETZ (*Jahrb. f. Min.*, 1879, 175).—On microscopical examination, the dolomite exhibited three kinds of structure, viz.:—1. Oolitic or oolithoidal structure. 2. Stratified structure. 3. Breccia-like structure. The first is simply a spheroidal occurrence of the crystalline individuals which the author believes to have been caused by movements taking place round about microlitic depositions of the dolomite substance, whilst the greater part of the surrounding mass was in a semi-fluid condition. The second formation is caused by the occurrence of alternate layers or strata of microcrystalline and macrocrystalline substance. The third formation is caused by the fragmentary occurrence of portions of microcrystalline and macrocrystalline substance together.

C. A. B.

Examination of Melaphyr from the Neighbourhood of Kleinschmalkalden. By F. M. WOLF (*Jahrb. f. Min.*, 1879, 162—163).—A very complete examination showed that all the specimens contained as essential constituents (wesentliche Bestandtheile) plagioclase, augite, and olivine embedded in a “base” of varying constitution, from which it was evident that all the rocks examined were true melaphyr. The author divides the melaphyrs of Kleinschmalkalden into two groups, viz.:—1. The rocks from the Reisigenstein, the Finsterliete, and the Linsenkopf. 2. The rock from the Eberhaidekopf. Analyses made of the above rocks showed that those of the first group contain 43 per cent. of silica and compounds of iron, whilst that of the second group contains 52 per cent. The rocks of the first group are characterised by a porphyritic occurrence of crystals of augite, olivine, and mica, which are surrounded by numerous small bands of felspar. These melaphyrs are *augitic melaphyrs*. The melaphyr from the Eberhaidekopf contains very little augite, no mica, and has a fine-grained structure.

C. A. B.

Petrographical Constitution of the Monzonite of Predrazzo. By V. HANSEL (*Jahrb. f. Min.*, 1879, 162).—Although monzonite belongs to the trias formation, it exhibits externally the characteristics of the old crystalline rocks, granite and syenite. Its microscopical enclosures make this resemblance all the more striking. On the other hand, its connection with more recent rocks is shown by the occurrence

of "glass enclosures" in the felspars. The varieties of monzonite can be arranged into two groups, in both of which plagioclase occurs together with orthoclase. The first group includes basic rocks, which (mineralogically speaking) correspond with diabase and gabbro, and contain from 40 to 50 per cent. of silica. The second group includes acid rocks, corresponding with syenite or diorite, and containing from 50 to 59 per cent. of silica. The last-mentioned group includes rocks consisting principally of hornblende, augite, and biotite, whilst those of the first group consist principally of augite or diallagite. The monzonite of Predrazzo is (mineralogically and geologically) almost identical with the monzonite of Monzoni, the only difference between them being the large occurrence of biotite in the rock of Predrazzo. C. A. B.

The Ferruginous Rocks of Ovifak and Assuk, in Greenland. By A. E. TÖRNEBOHM (*Jahrb. f. Min.*, 1879, 173—175).—The rocks which furnished the famous iron masses of Ovifak appear to be portions of a formation consisting principally of basalt, in which are enclosed fragments or portions of a dolerite and an anorthite rock containing graphite. The author found the native iron to occur principally in the dolerite or other enclosures in the basalt; he did not find it in the basalt alone. The dolerite consisted of plagioclase, augite, olivine, titanite, and a glassy "interpolation mass," and native iron occurs filling up the irregular interstices which exist between the above-mentioned mineral constituents of the dolerite. The native iron occurs as ductile grains, having an almost silver-white colour, also as dull grey almost lustreless particles, and black opaque masses (consisting probably of finely-divided iron, magnetite, and carbon), accompanied always by magnetic iron pyrites and a ferruginous silicate. The shining metallic particles do not consist of native iron alone, but in all probability contain schreibersite. The magnetic iron pyrites has a yellowish-grey colour, and contains particles of a sulphide which is easily decomposed (probably calcium sulphide or troilite). The ferruginous silicate varies in appearance, according to its more or less decomposed condition. It is rarely found fresh, and when it is in that condition it is isotropic, grass-green in colour, and is sharply defined from the "glassy mass" above mentioned. In the fresh condition, the silicate resembles chlorophane, whilst in the decomposed state it resembles hisingerite. This silicate occurs also in amygdaloidal nodules, analogous to the chlorophane nodules found in basalt and melaphyr, so that the mass filling up the irregular interstices between the various mineral constituents of the rock of Ovifak differs only from the corresponding mass of the basalts of other localities in containing native iron and magnetic iron pyrites. The round cavities in the dolerite of Ovifak are often filled with native iron (exhibiting sometimes Widmannstätten's figures) and magnetic iron pyrites, and it is quite evident that these globules of iron are not mechanical enclosures. The anorthite rock consists of a coarse-grained mass of asymmetrical felspars (anorthite and labradorite), graphite, and spinelle. It occurs sometimes in fragments interspersed in the basalt, and sometimes it is very intimately intermixed with the dolerite. Iron is found in this rock also, filling up the breccia-like inter-

stices. The rock of Assuk, in the Waigattet, consists of enstatite, asymmetrical felspar, and a glassy base. Between these constituents are interspersed numerous small grains of native iron, lumps of an opaque substance (most probably graphite), and some magnetic iron pyrites, whilst here and there a greenish mass was observed (ausfüllungsmasse), also larger nodules filled up zonally with viridite, quartz, or garnet. The Assuk rock, therefore, does not resemble that of Ovifak, and it cannot be a basalt, as it contains 56 per cent. of silica; it is probably a secondary molten mass. C. A. B.

A New Meteoric Mineral. By J. LAWRENCE SMITH (*Compt. rend.*, 90, 1460—1462).—The author has made a further examination of the mineral obtained from the meteoric shower at Iowa, 1879. The mineral forms projections on the surface of the stones. It has an easy cleavage, and on breaking presents an opalescent fatty appearance and a greenish-yellow colour. Its microscopic structure differs from that of olivine. Sp. gr. = 3·23.

The results of the analyses are as follows:—

	I.	II.	Oxygen.
SiO ₂	49·60	49·59	25·73
FeO	15·78	17·01	3·77
MgO	33·01	32·51	12·66

From these numbers the formula $2\text{SiO}_2\cdot\text{RO} + \text{SiO}_2\cdot 2\text{RO}$ may be deduced, which represents 2 mols. of enstatite or bronzite with 1 of olivine. For this mineral, the author proposes the name peckhamite. An account is also given of the meteoric shower. L. T. O'S.

Chemical Examination of the Grosslüder Mineral Spring at Salzschrif. By E. REICHARDT (*Arch. Pharm.* [3], 16, 208—216).—This spring is distinguished for its richness in carbonic anhydride, which constantly escapes; it discharges itself at a depth of about 1 metre from the surface, and therefore requires to be pumped. The samples received were slightly turbid, but became much more so after the escape of carbonic anhydride.

The analysis was made in the usual way, the following analytical details alone being noteworthy.

The *specific gravity* was taken after the escape of carbonic anhydride at the ordinary temperature (13·5° C.) had ceased.

Boric and *nitric acids* were absent.

Silicic acid was chiefly present in the deposit formed by standing; when hydrochloric acid in excess was added, this deposit entirely dissolved after a time, and silicic acid was then estimated by evaporation in the usual way.

Barium was detected in the sodium carbonate precipitate, but no strontium was found.

The direct results of analysis showed that 1,000 parts of water contained—

Cl.	Br.	P ₂ O ₅ .	SiO ₂ .	SO ₃ .	CO ₂ .	Na.	K.
9·653	0·1186	0·0008	0·3176	1·852	2·776	6·619	0·3146

Li.	CaO.	MgO.	SrO.	Fe ₂ O ₃ .	MnO.	Al ₂ O ₃ .
0.005	1.5869	0.5582	0.0009	0.0326	0.0044	0.0045.

Alkaline carbonates were absent, for the aqueous solution of the dried solid residue was not alkaline; but some of the potassium and sodium were present as organic salts, as was proved by igniting the residue, and also by permanganate. The following proportions of solid substances were calculated to have been present :—

	In one litre. grams.	In 1,000 grams. grams.
Sodium chloride	15.6835	15.4122
Potassium chloride	0.6102	0.5996
Lithium chloride	0.0033	0.0032
Magnesium chloride.....	0.0527	0.0518
Sodium bromide	0.1557	0.1530
Sodium (organic salts)	0.5020	0.4933
Calcium sulphate	1.6402	1.6118
Magnesium sulphate	1.3873	1.3633
Strontium sulphate	0.0016	0.0016
Calcium phosphate	0.0017	0.0017
Calcium carbonate	1.6730	1.6441
Magnesium carbonate	0.2173	0.2135
Ferrous carbonate.....	0.0481	0.0473
Manganous carbonate	0.0073	0.0072
Dissolved silica.....	0.3233	0.3176
Alumina.....	0.0046	0.0045
	<hr/> 22.3118	<hr/> 21.9257

Free carbonic anhydride at 11.5° C. and 760 mm. 1656.24 c.c. 1627.59 c.c. = 3.107 grams.
Specific gravity = 1.0176.

Subtracting from the total carbonic anhydride evolved on boiling that which had been expelled from the ferrous and manganous carbonates, the weight evolved from 1,000 grams of water would be 3.0864 grams.

The total solid residue from 1,000 grams of water dried at 100° C. weighed 21.860 grams, the loss on the weight calculated above being due to partial decomposition of the ferrous and manganous carbonates during evaporation and drying.

The analytical numbers obtained from four other Salzschlirf medicinal springs are tabulated with those yielded by the Grosslüder spring. The latter is remarkable as a saline spring, containing iron and much carbonic acid; it also contains much magnesium sulphate, whose unpleasant taste is masked by that of the carbonic acid; the water most closely resembles that of the Kissingen Racoczy, but is four times stronger. It remains clear for a considerable time after having been bottled. F. C.

Analysis of the Kanizer or Kainzen Spring. By F. HULWA (*J. pr. Chem.* [2], 22, 290—293).—This spring comes from the carbonaceous and dolomitic rocks not far from Partenkirchen, in the Partnach valley of the Bavarian highlands. Under these rocks lies a

stratum containing iron, lead pyrites, and different salts. The temperature of the water is 8° ; it is nearly clear, but a sediment forms on standing. It does not effervesce, but carbonic anhydride is evolved on heating. It has a distinct odour of sulphuretted hydrogen, and a faint sulphurous taste. The sediment consists of remains of phanerogams and cryptogams, together with organic detritus. The reaction is distinctly alkaline, especially on boiling. Sp. gr. 1.00074. It contains no free carbonic acid. Sulphuretted hydrogen is present only in minute quantities. Composition in 100,000 parts = 100 litres:—

a. Changeable Constituents.

Organic residue	1.200 parts.
Oxygen required for oxidation	0.288 "
Calculated for organic bodies	5.683 "
Ammonium nitrate	0.185 "

b. Mineral Constituents.

Sum of solid constituents: total residue = 58.6 parts containing:—

Sodium	31.303 parts.
Potassium	0.4915 "
Lithium	0.0023 "
Lime.....	0.5230 "
Magnesia	0.4967 "
Strontia	0.0042 "
Baryta.....	trace
Ferric oxide.....	0.075 "
Manganese dioxide.....	0.0008 "
Lead oxide	0.005 "
Copper oxide	0.0082 "
Silicic acid	1.0000 "
Sulphuric acid.....	2.646 "
Chlorine	0.7472 "
Bromine	0.002 "
Iodine	0.0045 "
Sodium carbonate	51.7538 "
Lithium	0.0057 "
Manganese carbonate....	0.1090 "
Manganous "	0.0124 "
Potassium sulphate.....	0.9082 "
Sodium "	0.8675 "
Calcium "	1.2700 "
Magnesium sulphate	1.4901 "
Strontium "	0.0070 "
Sodium chloride.....	1.2315 "
" bromide	0.0026 "
" iodide.....	0.0053 "
Lead oxide	0.0050 "
Copper oxide	0.0082 "
Silicic acid	1.0000 "
Total carbonic acid.....	21.9000 "
As bicarbonates.....	0.3700 "

The following points are characteristic of the Kainzen spring.

- (1.) The extreme softness of the water
- (2.) The relatively small quantity of mineral constituents.
- (3.) The occurrence of minute quantities of sulphuretted hydrogen.
- (4.) The absence of free carbonic acid.
- (5.) The combination of sodium carbonate, chiefly as mon carbonate.
- (6.) The relatively large proportion of sodium carbonate to the other constituents.

G. T. A.

Organic Chemistry.

Etherification of Hydrobromic Acid. By A. VILLIERS (*Compt. rend.*, **90**, 1488—1491).—The extent to which hydrobromic acid, when treated with absolute alcohol and a mixture of alcohol and water, undergoes etherification varies greatly with the temperature. Absolute alcohol, with different proportions of hydrobromic acid, and heated at different temperatures, gives the following results :—

		Percentage of acid etherified.	
		$\frac{1}{2}\text{HBr} + \text{C}_2\text{H}_5\text{O}$.	$\frac{1}{10}\text{HBr} + \text{C}_2\text{H}_5\text{O}$.
At ordinary temperature, limit 658 days		68.0	52.5
"	44°	79.6	59.9
"	100°	88.7	80.0

The percentage of acid converted into ether is not so great as that of the carbon acids, moreover, it is not fixed, but increases with the temperature.

These results show that combinations of alcohol with hydrobromic acid are formed analogous to hydrates.

The presence of water decreases the extent of etherification, and in large quantity prevents any action from taking place; the quantity of water required to prevent the action increases with the temperature. This is probably due to the formation of hydrates of hydrobromic acid, and the dissociation of these hydrates as the temperature is raised.

L. T. O'S.

Hydrate of Methyl Iodide. By FORCRAND (*Compt. rend.*, **90**, 1491—1493).—When a few drops of methyl iodide are placed in a tube and a strip of filter-paper is introduced, crystals are deposited on the edge of the paper after a short time. When all the iodide has disappeared from the glass a drop of water is seen at the end of each crystal, which increases as the crystal diminishes, and is finally absorbed by the filter-paper. During the formation of these crystals the temperature falls from about 16° to 15°. By passing a current of moist air through the iodide large quantities of the crystals are formed, but when dry air is used, no crystals are formed, notwithstanding the temperature sinks to a greater extent. The crystals melt at -4°, and therefore cannot be ice. The analyses show them to have the com-

position $(\text{CH}_3\text{I})_2\text{H}_2\text{O}$. Similar compounds of carbon bisulphide have been obtained by Berthelot (*Ann. Chim. Phys.* [3], **66**, 490).

L. T. O'S.

Compound of Ether with Phosphorus Pentachloride. By C. LIEBERMANN and L. LANDSHOFF (*Ber.*, **13**, 690—691).—A white crystalline compound is slowly deposited when absolute ether and finely-powdered phosphorus pentachloride are well shaken together. The composition of the crystals could not be ascertained with accuracy on account of their rapid decomposition by moisture; the analyses approximately agree with the formula $2\text{C}_4\text{H}_{10}\text{O} + 3\text{PCl}_5$ or $\text{P}_3\text{Cl}_{15}\text{C}_8\text{H}_{14}\text{O}_2$.

This substance is not a simple addition-product, since on adding water to it ether is not set free, but phosphoric and ethylphosphoric acids are produced. On distillation, it splits up into phosphorus trichloride and a mixture of chlorinated organic derivatives.

W. C. W.

Action of Methyl Bromide and Methyl Iodide on Monomethylamine. By E. DUVILLIER and A. BUISINE (*Compt. rend.*, **90**, 1426—1427).—When equal molecular proportions of methyl bromide and monomethylamine, dissolved in methyl alcohol, are heated at 100° , the products of the reaction consist of unaltered monomethylamine, small quantities of di- and tri-methylamine, and large quantities of tetramethylammonium bromide. A similar result is obtained by treating methylamine with methyl iodide, the reaction being very violent. These reactions are similar to that of methyl nitrate on monomethylamine, and they are all comparable with the action of methyl iodide on ammonia.

L. T. O'S.

Amylamines from Inactive Amyl Alcohol. By R. P. PLIMPTON (*Compt. rend.*, **91**, 433—435).—A quantity of inactive amyl chloride was prepared by Le Bel's process (*Compt. rend.*, **77**, 1021) from the mixture of active and inactive alcohols resulting from fermentation. The chloride prepared in this way (b. p. 100.5°) was without action on polarised light when examined in a tube 1 meter long. Heated at 150° in a digester for one or two hours with a little more than its own weight of a saturated solution of ammonia in alcohol, it was converted into a crystalline mass. From this the amyamine was separated in the usual manner, and purified by repeated rectification over potash. It boils at 96.5° under a pressure of 766 mm. (Wurtz, 95° ; Brazier and Gosleth, 93° ; Custer, $92-93^\circ$): a trace of moisture lowers the boiling point $2-3^\circ$. Sp. gr. at $22.5^\circ = 0.7517$.

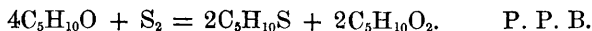
Amylamine hydrochloride (inactive) is very soluble in hot alcohol, insoluble in ether. The platinochloride separates from hot water in plates. The aurochloride is obtained by slow evaporation in clinorhombic crystals, resembling those of augite. It is soluble in alcohol and ether. The residue from the distillation of the amyamine contains inactive diamylamine and triamylamine. These were separated as far as possible by fractional distillation, converted into hydrochlorides, and treated with ether, which dissolves triamylamine hydrochloride only.

Diamylamine, prepared from the hydrochloride purified by crystallisation from water, boils at 185° (Hofmann, 176° ; Custer, 187° , for the product obtained from nitrosodiamylamine). The *hydrochloride* forms splendid plates, sparingly soluble in hot water. The *platinochloride* crystallises well, is soluble in alcohol, but not in water. The *aurochloride* forms needles soluble in alcohol, insoluble in water.

Triamylamine boils at 237° (uncorr.) (Hofmann, 256°). It is an oleaginous liquid, insoluble in water. The *hydrochloride* separates from ether in slender prisms. It is very soluble in ether and alcohol, less soluble in water; melts below 100° . The *platinochloride* is insoluble in water. The *aurochloride* crystallises from alcohol in needles, insoluble in water.

1 kilo. of inactive amylamine chloride gave 15–20 grams of amylamine, 150 grams of diamylamine, and about 130 grams of triamylamine.
J. M. H. M.

Thiovaleraldehyde. By G. A. BARBAGLIA (*Ber.*, **13**, 1574).—Schroeder (*Ber.*, **4**, 402) describes a solid thiovaleraldehyde obtained by acting on valeraldehyde with sulphuretted hydrogen. By heating sulphur and valeraldehyde at 250° in sealed tubes, a liquid valeraldehyde, $C_5H_{10}S$, has been obtained. It is a clear liquid of exceedingly disagreeable odour, resembling that of garlic. It boils at 114 – 115° ; is insoluble in water, and easily miscible with alcohol or ether. Valerianic acid is formed during the reaction, which may be expressed as follows:—



Action of Chlorine on Di-isopropylketone. By G. A. BARBAGLIA and P. GUCCI (*Ber.*, **13**, 1570–1571).—*Monochloro-di-isopropylketone*, $C_7H_{13}ClO$, is obtained by acting on dry di-isopropylketone with dry chlorine; it is a liquid having an odour resembling that of camphor and turpentine, and boils at 141 – 142° .

Dichloro-di-isopropylketone, $C_7H_{12}Cl_2O$, is obtained by passing chlorine into the ketone and water; it is a liquid having an odour of turpentine, and boils at 175 – 176° .

Trichloro-di-isopropylketone, $C_7H_{11}Cl_3O$, is obtained by the action of chlorine on the vapours of di-isopropylketone; it is a colourless liquid, which blackens on standing, and has a penetrating odour; it boils at 228 – 229° .

The further action of chlorine on di-isopropylketone is attended with the production of resinous bodies.
P. P. B.

Constitution of Lactones. By J. BREDT (*Ber.*, **13**, 748–749).—The author finds that isocaproic acid is converted, by oxidation with potassium permanganate, into the lactone, $C_6H_{10}O_2$, identical with the lactone obtained by heating terebic acid, and infers that the lactones ought to be regarded as the phthalides of the fatty series.

W. C. W.

Propylacetal and Isobutylacetal. By J. GIRARD (*Compt. rend.*, **91**, 629–631).—Propylacetal is obtained by passing a current of non-inflammable phosphoretted hydrogen for several hours into a mixture

of aldehyde and propylic alcohol. After the products have been washed with water and dried by contact with calcium chloride, the propylacetal is isolated by fractional distillation. It is a colourless liquid, b. p. $146-148^{\circ}$; insoluble in water, but soluble in alcohol and in ether; sp. gr. at $22.5^{\circ} = 0.825$. It does not reduce ammoniacal silver nitrate, and is not acted on by potassium, or by a boiling solution of potash. Concentrated hydrochloric acid dissolves it without coloration; strong sulphuric acid carbonises it in the cold.

Isobutylacetal is obtained in a similar manner, and its properties are similar to those of propylacetal; b. p. $168-170^{\circ}$; density at $22^{\circ} = 0.816$. R. R.

Dry Distillation of Calcium Isobutyrate. By G. A. BAGLIA and P. GUCCI (*Ber.*, **13**, 1571—1572).—Amongst the products obtained by the distillation of calcium isobutyrate, beside di-isopropylketone, the authors have found water, isobutyric acid, isobutylaldehyde (Popoff, *Ber.*, **6**, 1255), methylpseudobutylketone (described by Butlerow, *Ber.*, **7**, 729), and a compound having the empirical formula $C_7H_{12}O$. This compound is a liquid having an odour resembling that of peppermint, and boils at $150-152^{\circ}$.

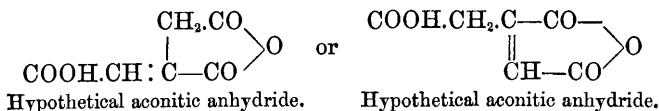
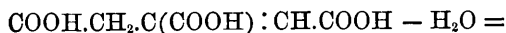
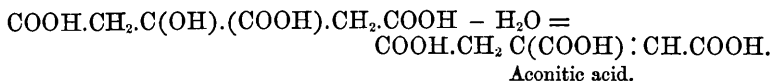
P. P. B.

Itaconic Anhydride. By R. ANSCHÜTZ and W. PETRI (*Ber.*, **13**, 1539—1540).—It has been shown in former communications (*Ber.*, **10**, 325 and 1881) that dibasic acids are easily converted into their anhydrides by the action of acetic chloride, and that whilst fumaric acid is not attacked by this reagent, maleic acid is converted into its anhydride (*Ber.*, **12**, 2281). Itaconic acid heated in the water-bath with acetic chloride is also converted into the anhydride.

Itaconic anhydride, $C_5H_4O_3$, crystallises from glacial acetic acid in colourless, transparent, compact columnar crystals; it melts at 68° and distils at $139-140^{\circ}$ under a pressure of 30 mm. If distilled under the ordinary pressure, it is converted into citraconic anhydride. Itaconic anhydride, mixed with glacial acetic acid or citraconic anhydride, remains liquid for a considerable length of time when cooled below its melting point. When dissolved in warm water, it is converted into itaconic acid. It crystallises from chloroform in clear prismatic crystals, belonging to the rhombic system, which become dull on exposure to the air. It resembles maleic anhydride in appearance, and in its behaviour with acetic acid and chloroform.

P. P. B.

Decomposition of Citric Acid by Distillation. By R. ANSCHÜTZ (*Ber.*, **13**, 1541—1543).—When citric acid is distilled, the portion coming over between $200-215^{\circ}$ separates into two layers. If these be separated, and the heavier portion fractionated under reduced pressure (30 mm.), the following three fractions are obtained:—(1), 120° ; (2), $120-130^{\circ}$; (3), $130-140^{\circ}$. The author finds that fractions (2) and (3) consist chiefly of itaconic anhydride, whilst the first fraction consists of citraconic and itaconic anhydrides. The formation of these anhydrides is explained as follows:—



The first aconitic anhydride loses CO_2 and gives citraconic anhydride, having the formula $\begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 : \text{C} - \text{CO} \end{array} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}$; whilst the second would yield CO_2 and itaconic anhydride, to which the constitutional formula $\begin{array}{c} \text{CH}_3 \cdot \text{C} - \text{CO} - \\ || \\ \text{CH} - \text{CO} \end{array} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}$ is attributed.

The author has shown (preceding abstract) that itaconic anhydride is converted by heat into citraconic anhydride. Its formation in the above case is accounted for by its being carried over by the current of carbonic anhydride produced in the above decomposition.

P. P. B.

Mucobromic Acid. By H. B. HILL (*Ber.*, **13**, 734—739).—By the action of dry bromine (1 mol.) on mucobromic acid (2 mols.) at 130 — 140° , a mixture of bromomucobromic and dibromosuccinic acids with dibromomaleic anhydride is produced. The acid which is formed by dissolving the anhydride in water is identical with Kekulé's dibromomaleic acid. The dibromo-fumaric acid which Limpricht and Delbrück (*Annalen*, **165**, 293) obtained by heating mucobromic acid with bromine and water is also identical with dibromomaleic acid. Mucobromic acid also yields dibromomaleic acid on oxidation with dilute nitric acid.

W. C. W.

Influence of Isomerism of Alcohols on the Formation of Ethereal Salts. By MENSCHUTKIN (*Ann. Chim. Phys.* [5], **20**, 289—361).—The author has endeavoured to throw light on the relations of isomeric alcohols by a quantitative study of the formation of ethereal salts by heating the various alcohols with the same acid. On a future occasion he proposes to extend the research by heating the same alcohol with various acids. The present paper has reference to the reaction of acetic acid with primary, secondary, and tertiary alcohols and with phenols, a short account of which has already appeared (this Journal, 1879; Abstr., 36, 214, and 215). Similar experiments were carried out by Berthelot and Péan de St. Gilles in 1862 and 1863, but at that time the isomeric alcohols were little known.

Method of Experiment.—A certain quantity of the alcohol was weighed out, and the theoretical equivalent of acetic acid added from a dropping pipette. About 0.5 gram of the mixture was then weighed

carefully into a tube of 5 mm. diameter, of such a length that the mixture occupied half to two-thirds of the volume. The tube was sealed and suspended in a glycerol-bath, kept constant at 154°. At the end of a certain number of hours the tubes were withdrawn from the bath and broken into stoppered flasks, containing about 50 c.c. of alcohol. A few drops of an alcoholic solution of rosolic acid were added, and the free acetic acid titrated with standard baryta-water. The observations were made with a view to obtaining two sets of numbers—(1) *the initial rate of etherification*, expressed by the percentage of acid found combined with the alcohol at the end of the first hour; and (2) *the limit of etherification*, expressed by the percentage of acid converted into an acetate when etherification ceased. The error of experiment for the former determination averaged ± 1 per cent. from the mean; for the latter, ± 0.4 per cent. from the mean.

Acetic Ethers of the Primary Alcohols.—The alcohols, first purified as far as possible, were in all cases dried over caustic baryta. The following mode of procedure was adopted, as it was the only one that afforded a guarantee of the completeness of the desiccation:—The whole quantity of purified alcohol was dried over baryta, distilled, and an etherification assay made; the remainder was treated a second time with baryta and distilled, and another etherification essay made. If the second really agreed with the first, the experiments were assumed to be correct; if not, the drying and testing were repeated until two successive series of results showed no appreciable difference. The results obtained in this way have already been given (*loc. cit.*, p. 36).

With regard to the limit of etherification, Berthelot and St. Gilles concluded that “the equivalent proportions of acid and alcohol that enter into combination are almost independent of the special nature of the acid or alcohol.” The results obtained by the author are opposed to this conclusion, and show on the other hand that (1) methyl alcohol is distinguished from all other alcohols by its high limit; (2) for the other members of the $C_nH_{2n+1}.HO$ series, the limit increases with increase of molecular weight, but is not influenced by isomerism; (3) alcohols of the unsaturated series have a considerably lower limit than those of the $C_nH_{2n+1}.HO$ series; the limit of allyl alcohol, for example, being 7.5 per cent. less than that of propyl alcohol.

Acetic Ethers of the Secondary Alcohols.—The author's mean results may be exhibited briefly in the following table, similar to that for the primary alcohols:—

Alcohol.	Initial rate.	Limit.
Dimethylcarbinol (isopropyl alcohol).	26.53	60.52
Ethylmethylcarbinol (secondary butyl alcohol)	22.56	50.28
Isopropylmethylcarbinol	18.95	59.31
Diethylcarbinol	16.93	58.66
Hexylmethylcarbinol (capryl alcohol).	21.19	62.03
Ethyl vinyl carbinol	14.85	52.25
Diallylcarbinol	10.31	50.12

Both the initial rate and the limit of etherification are thus much lower for secondary than for primary alcohols. Comparing the former amongst themselves, the highest initial rate is that of dimethylcarbinol; whilst the two other alcohols of similar structure, ethylmethylcarbinol and hexylmethylcarbinol, have a lower rate almost identical in the two cases. The influence of isomerism in lowering the rate is shown by comparing isopropylmethylcarbinol (18.95) with diethylcarbinol (16.93). The relative initial rate is lowered by increase of molecular weight and by isomerism, as the following numbers show:—Dimethylcarbinol, 43.85; ethylmethylcarbinol, 38.10; hexylmethylcarbinol, 34.16; isopropylmethylcarbinol, 31.95; diethylcarbinol, 28.86. The absolute and relative rates are also lower for alcohols containing unsaturated radicles than for those containing only C_nH_{2n+1} radicles, but this difference is not so great as it is with the primary alcohols. The limit of etherification of secondary alcohols does not show an increase with increase of molecular weight, but is considerably lower for the non-saturated than for the saturated series.

Acetic Ethers of Tertiary Alcohols.—The reaction of tertiary alcohols with acetic acid differs from that of primary and secondary alcohols, being generally complicated by dissociation of the compound ether into olefine and acid, and the re-formation of the tertiary alcohol by combination of the olefine with water in presence of acid; and perhaps combination of the olefine with acid to form the ethereal salt. All these reactions are limited. After heating the mixture for a certain time, equilibrium is established, which, as the formation of the olefine is a case of dissociation, depends on the temperature.

1. *Formation of the Compound Ether with Elimination of Water.*—On account of the partial dissociation of the ethereal salt into hydrocarbon and acid, the limit of etherification cannot be ascertained with accuracy; but it is very much lower than in the case of primary or secondary alcohols, and is attained in a comparatively short time. The quantity of acid etherified at the end of 24 hours, compared with the mean limit and the initial rate (absolute) of etherification, have already been given (*loc. cit.*, p. 216).

2. *Decomposition of the Ethereal Salt by the Water formed in the Reaction.*—In consequence of the relatively larger quantity of water formed during the etherification of tertiary alcohols, this reaction proceeds to a much greater extent than in the case of primary and secondary alcohols.

3. *Dissociation of the Compound Ether into Olefine and Acid.*—This reaction occurs in all the cases studied, and reaches a limit dependent on the temperature employed. Equations representing the equilibrium of the system formed by a molecular mixture of trimethylcarbinol and acetic acid at 155° have been given (*loc. cit.*, p. 216).

The author gives in detail the analytical data from which these equations are deduced. The polymerisation of the olefines under the influence of sulphuric acid is explained by the author as the dissociation of sulphovinic ethers of the tertiary alcohols, which it is known are produced from these hydrocarbons by fixation of water.

Acetic Ethers of Phenols.—The results of experiments with phenol, paracresol, thymol, and α -naphthol have been given (*loc. cit.*, p. 217).

They show a striking resemblance in this respect to tertiary alcohols, with which the author suggests they should be classed; their similarity in structure is shown by the position of the hydroxyl group, this being in both cases attached to a carbon atom, whose remaining affinities are satisfied by carbon atoms. The continuity between the aromatic and other series is again shown by these experiments. No dissociation of the acetic ethers of this class was observed at the temperature (155°) employed. The general conclusions to be deduced from the whole of the author's experiments have been pointed out in the remarks on each class.

J. M. H. M.

Influence of Isomerism of Monobasic Saturated Acids on Etherification. By N. MENSCHUTKIN (*Bull. Soc. Chim.* [3], **34**, 87—388).—The relative initial velocity (at the end of one hour at 155° C.) and limit of etherification of primary, secondary, and tertiary monobasic fatty acids are compared:—

<i>Primary acids.</i>	Initial velocity.	Limit.
Formic acid.....	61·69	64·23 (at 100° C.)
Acetic acid	44·36	67·38 (at 155 C.)
Propionic acid	41·18	68·70 ,,
Normal butyric acid....	33·25	69·52 ,,
Normal caproic acid....	33·08	69·81 ,,
Normal caprylic acid	30·86	70·87 ,,
<i>Secondary acids.</i>		
Isobutyric acid	29·03	69·51 ,,
Methylethyl acetic acid ..	21·50	73·71 ,,
<i>Tertiary acids.</i>		
Trimethyl-acetic acid....	8·25	72·65 ,,
Dimethylethyl-acetic acid	3·45	74·15 ,,

V. H. V.

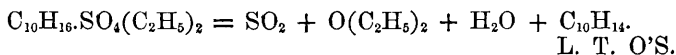
Oxidation-products of Dimethyluric Acid. By C. F. MABERY and H. B. HILL (*Ber.*, **13**, 739—740).—Methylalloxan and methylcarbamide are formed by the oxidation of dimethyluric acid with nitric acid or with hydrochloric acid and potassium chlorate. In the latter case a small quantity of a compound having the composition $C_6H_6N_2O_3$ is produced. This substance crystallises in prisms (m. p. 160°) which are sparingly soluble in cold water. It appears to act as an acid.

Methylparabanic acid (m. p. 149°) is formed from dimethyluric acid by long-continued boiling with nitric acid.

W. C. W.

Conversion of Terebenthene into Cymene. By BRUÈRE (*Compt. rend.*, **90**, 1428—1429).—When terebenthene is dropped slowly into boiling sulphuric acid mixed with 2 mols. of water, a mixture of cymene with unaltered terebenthene and water distils over. This unaltered terebenthene is polymerised by agitation with concentrated sulphuric acid and the cymene purified by a final distillation. The water is separated out from the product, the sulphurous acid neutralised with sodium carbonate, and the remaining liquid dried and fraction-

ally distilled. Unsuccessful attempts were made to substitute other bodies for sulphuric acid, which is very violent in its action, but on heating 1 mol. of terebenthene with 1 mol. of ethyl sulphate at 120° for 10—15 hours, the mixture assumes a violet colour, and contains cymene, ether, and sulphurous acid. By allowing terebenthene and ethyl sulphate to remain in contact for some time at 100°, the mixture gradually becomes homogeneous. The liquid produced is heavier than water, is stable at the ordinary temperature, of a lemon-yellow colour, and peculiar odour. When cooled to -20° the mixture separates into two layers, one of terebenthene, the other of ethyl sulphate. The homogeneous solution appears to be a very unstable combination of terebenthene and ethyl sulphate, $C_{10}H_{16}.SO_4(C_2H_5)_2$, which readily splits up into cymene and ether—



Remarks on Kelbe's Discovery of a New Cymene in Light Resin Oil (Resin Spirit). By H. E. ARMSTRONG and W. A. TILDEN (*Ber.*, 13, 1548—1549).—The authors draw attention to the fact that they have been engaged for some time in the investigation of "resin spirit," and have already published some account of their results (this *Journal*, *Trans.*, 1879, 275, and *Ber.*, 12, 176). Whilst acknowledging the right of Kelbe to continue the investigation of the new hydrocarbon, the authors wish to reserve the further study of resin spirit.

P. P. B.

Synthesis of Hexmethylbenzene and of Mellitic Acid. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, 91, 257—260).—In a previous paper (*Compt. rend.*, 84, 1394), the authors announced the formation of tetramethylbenzene by passing a current of methyl chloride through a warm mixture of benzene with aluminium chloride; at the same time they suspected the presence of pentamethylbenzene and hexmethylbenzene amongst the products. By operating with toluene instead of benzene they have succeeded in preparing these two compounds in considerable quantity.

On purification by fractional distillation and pressure of the solid product, three distinct compounds are obtained, boiling constantly at 190°, 225°, and 264°, and melting at 110°, 50°, and 164° respectively. The first of these bodies is tetramethylbenzene, the second pentamethylbenzene, and the third hexmethylbenzene. The vapour-densities of the two latter are 5.27, 5.73 (experiment), corresponding with 5.12 and 5.61 (theory). Attempts were also made to purify these substances by fractional crystallisation from alcohol and by the action of strong sulphuric acid, which attacks the less methylated benzene hydrocarbon first. Neither of these methods was successful. By oxidising hexmethylbenzene with dilute nitric acid or with nitric acid and potassium permanganate, a mixture of acids was obtained, amongst which there appeared to be a small quantity of mellitic acid. When potassium permanganate alone was used for the oxidation, and the action allowed to spread over several months, a much larger quantity of mellitic acid (as potassium mellitate) was obtained, which

was identified by its reactions with salts of barium, calcium, zinc, copper, silver, and magnesium, and by analysis of the silver salt.

J. M. H. M.

Paraditolylnitrosamine. By A. LEHNE (*Ber.*, **13**, 1544—1545).—Gerber (Dissertation, *Zurich*, 1874) and J. Cosack (*Ber.*, **13**, 1092) have already obtained this body. The author prepares it by heating ditolylamine in alcohol with hydrochloric acid and then adding a solution of sodium nitrite. It is insoluble in water, but soluble in ether, benzene, and light petroleum, and sparingly so in alcohol. It crystallises from light petroleum in golden-yellow rhombic crystals. Bromine acts on this nitrosamine, forming tetrabromditolylamine, $(C_7H_5Br_2)_2NH$, which melts at 162° . It has been described by Gerber (*loc. cit.*). It may also be obtained directly from ditolylamine.

Hexnitroditolylamine, $C_{14}H_8(NO_2)_6NH$, is prepared by the careful nitration of paraditolylnitrosamine, it may also be obtained from paraditolyamine. It crystallises from glacial acetic acid in yellow crystals, which melt at 258° , and is sparingly soluble in the ordinary solvents. Its acetic acid solution on reduction with zinc-dust gives a deep-red coloration. Hexnitroditolylamine corresponds with the nitro-derivative of diphenylamine, used as a dye under the name of "aurantia."

P. P. B.

Paraditolylyhydrazine. By A. LEHNE (*Ber.*, **13**, 1546—1547).—This compound is prepared by the reduction of ditolylnitrosamine with zinc and acetic acid in a manner analogous to Fischer's preparation of diphenylhydrazine (*Hydrazinverbindungen*; München).

Paraditolylyhydrazine, $(C_7H_7)_2N_2H_2$, crystallises from benzene in colourless leaflets, melting at 171 — 172° . It is easily soluble in alcohol and benzene, sparingly in ether, and almost insoluble in light petroleum. When dry it does not change on exposure to the air, its chloroform solution, however, becomes blue under these circumstances.

The *hydrochloride*, $(C_7H_7)_2N_2H_2.HCl$, is an unstable salt; it crystallises in slender colourless needles. It is easily soluble in water, and its solution on cooling decomposes into basic salt and free acid, on warming the salt is again formed.

Monobenzoylditolylhydrazine, $(C_7H_7)_2N_2H.C_6H_5CO$, is obtained by acting on a solution of the base in benzene with benzoic chloride. It crystallises in slender colourless needles, melting at 186.5° . Its solution in benzene becomes dark green on exposure to the air. Nitrous acid converts ditolylyhydrazine into ditolylnitrosamine. Ditolylyhydrazine is converted by bromine into tetrabromoditolylamine, and by nitric acid into hexnitroditolylamine. Oxidising agents, such as ferric chloride or mercuric oxide, convert it into ditolylamine.

P. P. B.

Azo-derivatives. By J. H. STEBBINS (*Ber.*, **13**, 715—718).—*Azobenzenehydroxybenzoic acid*, $PhN_2.C_6H_3(OH).COOH$, is deposited in orange-coloured needles from an alkaline mixture of diazobenzene nitrate and salicylic acid. The crystals are soluble in alcohol and insoluble in water. A sulphonic acid is obtained by the action of sulphuric acid.

Phloroglucinparazobenzenesulphonic acid, $C_6H_4(HSO_3).N_2.C_6H_2(OH)_3$, crystallises in yellow plates, having a metallic lustre. The sodium salt is prepared by mixing sodium paradiazobenzenesulphonate with an alkaline solution of phloroglucin. The precipitated salt is purified by solution in hot water and reprecipitation by sodium chloride.

Azobenzene diamidotoluene, $C_6H_5.N_2.C_6H_2Me(NH_2)_2$, is obtained in yellow needles soluble in alcohol, by treating with ammonia the product of the action of α -toluylenediamine on diazobenzene. This base forms a hydrochloride, crystallising in orange-coloured needles, which dissolve freely in water. With an excess of hydrochloric acid, an unstable scarlet coloured crystalline compound is produced. The hydrochloride also forms crystalline double salts with metallic chlorides.

Diamidoazonaphthalene, $C_{10}H_7.N_2.C_{10}H_5(NH_2)_2$, prepared from diazonaphthalene nitrate and diamidonaphthalene, unites with acids to form brown coloured salts.

Azobenzenecresolsulphonic acid, $C_6H_5.N_2.C_6H_2Me(HSO_3).OH$, obtained by the action of diazobenzene nitrate on an alkaline solution of cresolsulphonic acid, forms brown, needle-shaped crystals, having a strong metallic lustre. It dissolves in alcohol, forming a solution which dyes silk or wool yellow.

W. C. W.

Action of Hydrochloric Acid on Organic Amides (Preliminary). By L. SCHULERUD (*J. pr. Chem.* [2], 22, 288—290).—When amidobenzoic acid is heated in a stream of dry hydrochloric acid gas, ammonium chloride sublimes, and a solid amorphous residue remains in the retort. This body is unacted on by the ordinary solvents, but is soluble in concentrated sulphuric acid, and is precipitated from the solution unchanged by water. It does not melt when heated, but chars and decomposes. Analysis gave no satisfactory result.

When heated with hydrochloric acid gas, salicylamide splits up into disalicylamide and ammonia. A part of the amide sublimes unaltered, water and phenol are also evolved. Disalicylamide is a yellowish-white, asbestos-like body, consisting of small, woolly needles, insoluble in water, but tolerably soluble in hot alcohol and acetic acid. The alcoholic solution gives a yellowish-red to blood-red precipitate with ferric chloride. The diamide (m. p. 197—199°) dissolves in alkalis with a yellow colour, and forms compounds with metals. The silver compound, $(C_6H_4(OH).CO)_2NAg$, is crystalline, and of a yellow colour.

Salicylamide absorbs hydrochloric acid slowly at ordinary temperatures, with formation of a compound, from which a stream of dry air gradually expels the gas in the cold. The gas is also expelled by warming the compound either alone or with water or alcohol. When hydrochloric acid is passed into a solution of salicylamide in dry ether, brilliant acicular crystals are formed, consisting of $2C_6H_4(OH).CONH_2 + HCl$. Hydroxybenzamide is obtained by leaving the ether of hydroxybenzoic acid in contact with strong ammonia. It forms colourless thin plates (m. p. 167° uncorr.), which dissolve readily in hot water and in alcohol.

G. T. A.

Alphatoluylamide. By C. L. REIMER (*Ber.*, **13**, 741).—In the preparation of benzyl cyanide by the action of potassium cyanide on benzyl chloride, α -toluylamide is obtained as a bye-product. The toluylamide is found in the retort, after the benzyl cyanide has been distilled over in a current of steam. W. C. W.

Phenyl- and Toly-thiocarbimide Glycollide. By M. VÖLTZKOW (*Ber.*, **13**, 1579—1580).—The author describes some homologues of phenylthiocarbimide-glycollide (this Journal, **38**, 659), which have been obtained in a similar manner.

Paratolythiocarbimide-glycollide, $C_7H_7N : C < \begin{smallmatrix} S.CH_2 \\ \text{---}O\text{---} \end{smallmatrix} > CO$, obtained from paratolythiocarbimide and monochloracetic acid; it crystallises from hot water in small leaflets or needles (m. p. 162°), easily soluble in the ordinary solvents. It is decomposed by boiling with baryta-water in a manner analogous to the phenyl-derivative, yielding paratoluidine, barium carbonate, and barium thioglycollate.

Orthotolythiocarbimide-glycollide is prepared in a manner similar to the para-compound; it crystallises in white, shining needles (m. p. 120°), and is easily soluble in the ordinary solvents. By boiling with baryta-water, it is resolved into orthotoluidine, carbonic anhydride and thio-glycollic acid.

When phenyl- or tolyl-thiocarbimide is heated with monochloracetic acid alone, then compounds are formed having the formulæ C_8H_8NOCl and $C_9H_{10}NOCl$. The former is obtained from phenylthiocarbimide, the latter from tolythiocarbimide. P. P. B.

Guanythiocarbamide and some Guanylguanidines. By E. BAMBERGER (*Ber.*, **13**, 1580—1584).—The author regards Rathke's thiodicyandiamine (*Ber.*, **11**, 967), guanythiocarbamide, and the compound described by the same author (this Journal, **34**, 804), having the formula $NHPh.CS.NPh.C(NH_2) : NHPh$, as a triphenylated guanythiocarbamide. The following derivatives of this guanythiocarbamide have been obtained:—

Guanylphenylthiocarbamide, $C_8SN_4H_{10}$, prepared by acting upon guanine carbonate with phenylthiocarbimide, crystallises in white, shining, strongly refractive, monoclinic crystals (m. p. 175 — 176°). It dissolves in alcohol, yielding an alkaline solution. It is a base, and is easily soluble in acids. Its *hydrochloride*, $C_8SN_4H_{10}.HCl$, crystallises in long, silky needles, and is more easily soluble in alcohol than water; on warming, its aqueous solution evolves sulphuretted hydrogen. This solution gives a yellow precipitate with platinum chloride, and a dirty violet precipitate with copper sulphate, becoming black on boiling, owing to its conversion into sulphide.

The *picrate*, $C_8SN_4H_{10}.C_6H_2(NO_2)_3OH$, crystallises in yellow needles. The *oxalate* crystallises in white, shining scales. The *sulphate* crystallises in shining leaflets; its aqueous solution decomposes when warmed, forming a yellow powder, which is soluble in alcohol. By heating with hydrochloric acid at 185° , the base is resolved into carbonic anhydride, sulphuretted hydrogen, aniline, and perhaps

guanidine, and may therefore be represented by either of the two following formulæ:—



Phenylguanylguanidine, $\text{NH:C(NHPh).NH.C(NH}_2\text{):NH}$. The nitrate of this base is obtained by treating guanylphenylthiocarbamide with ammoniacal silver nitrate; it has the composition $\text{C}_8\text{H}_6\text{H}_{12}\text{O}_3$, and melts at $208\text{--}209^\circ$. It is easily soluble in alcohol and water, and the base is precipitated from its aqueous solutions in a flocculent state by soda, but becomes crystalline on standing.

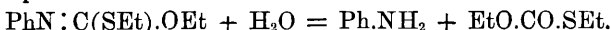
When guanylphenylthiocarbamide is treated with an alcoholic solution of mercuric chloride, the hydrochloride $\text{C}_8\text{N}_5\text{H}_4\text{.HCl}$ is obtained; and the sulphate is obtained by treatment with silver sulphate. When treated with moist silver oxide, the hydrochloride yields the free base $\text{C}_8\text{H}_5\text{H}_{11}$, which crystallises in white leaflets; it is easily soluble in alcohol and in water, and is precipitated from its aqueous solutions by soda.

Diphenylguanylguanidine, $\text{NPh:C(NHPh).NH.C(NH}_2\text{):NH}$. The nitrate of this base is obtained by treating guanylphenylthiocarbamide with silver nitrate in presence of aniline. It crystallises from water in shining white needles united in groups (m. p. 231°). The free base is precipitable on adding soda to the aqueous solution of the nitrate. The base is unchanged by exposure to the air, and is more easily soluble in alcohol than water, forming an alkaline solution. P. P. B.

Constitution of the Thiourethanes. By C. LIEBERMANN (*Ber.*, 13, 682—689).—The acid nature of *phenylthiourethane*, PhN:C(SH).OEt , is shown by the fact that this substance dissolves in dilute solutions of potash, soda, or baryta, and is reprecipitated from these solutions on the addition of an acid. Phenylthiourethane forms metallic compounds, which are obtained as crystalline precipitates when certain metallic salts are added to its alcoholic solution, e.g., $\text{PhNC:(Sph).OEt} + \text{H}_2\text{O}$; PhN:C(SAg).OEt , and $\text{PhN:C(SHgCl.HCl).OEt}$. By the action of methyl and ethyl iodides on the silver salt at 100° , methyl and ethyl derivatives have been prepared. PhN:C(SMe).OEt is an oily liquid (b. p. $260\text{--}265^\circ$), soluble in strong hydrochloric acid, but reprecipitated on dilution with water. The hydrochloric acid solution gives with platinum chloride an orange-coloured crystalline precipitate, which is sparingly soluble in cold alcohol.

Ethylphenylthiourethane, PhN:C(SET).OEt , when freshly prepared, is an oily liquid (b. p. 275°), which slowly solidifies to a crystalline mass (m. p. 30°). The platinochloride resembles that of the preceding compound.

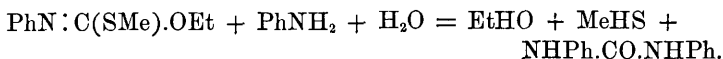
The ethyl compound is decomposed by the action of dilute sulphuric acid at 200° into aniline and ethyl thiocarbonate, according to the following equation:—



When phenylthiourethane is heated with dilute sulphuric acid, it splits up into aniline, alcohol, carbonic oxide, and sulphuretted hydrogen.

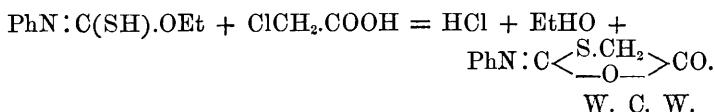


On boiling a mixture of methylphenylthiourethane, aniline, and alcohol in a flask connected with an upright condenser, methylmercaptan and diphenylcarbamide are produced.

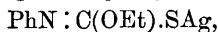


If alcoholic ammonia is substituted for aniline in the preceding experiment, aniline and monophenylguanidine will be produced.

From the preceding reactions the author concludes that thiourethanes have the constitution $\text{R.N:C} < \begin{smallmatrix} \text{SM} \\ \text{OR} \end{smallmatrix}$. The formation of phenylthiocarbamidoglycollide by the action of monochloroacetic acid on phenylthiourethane, must be represented as follows:—



Para- and Ortho-tolylthiourethanes. By C. LIEBERMANN and S. NATANSON (*Ber.*, **13**, 1575—1579).—In favour of the views already advanced by one of the authors (*Ber.*, **13**, 682), as to the constitution of phenylthiourethane, the formation of phenylurethane sulphide, $\text{NPh:C(OEt).S}_2\text{C(OEt):NPh}$, is cited. This compound is obtained by decomposing silver phenylthiourethane,



with iodine. It crystallises from alcohol in colourless rhombic prisms, and melts at 102° .

Paratolylthiourethane, $\text{C}_7\text{H}_7\text{N:C(OEt).SH}$, is prepared in a manner similar to the phenyl derivative, viz., by heating paratolylthiocarbamide with alcohol at 130° . It forms colourless transparent crystals, melting at 87° .

Orthotolylthiourethane is prepared from the orthotolylthiocarbamide. It is an oil.

Both the tolylthiourethanes are soluble in dilute alkalis, and are reprecipitated by acids. Ammoniacal silver nitrate precipitates the silver salts from alcoholic solutions of the tolylthiourethanes. The methyl and ethyl derivatives of these tolylthiourethanes have been obtained by decomposing the silver salts with methyl and ethyl iodides respectively. These derivatives may also be obtained by boiling solutions of the tolylthiourethanes in caustic alkalis with methyl or ethyl iodide. The methyl and ethyl salts are oils, which distil above 250° without decomposition.

The ethyl derivative of paratolylthiourethane yields mercaptan when heated with ammonia at 150° ; with dilute sulphuric acid at 200° , paratoluidine sulphate and ethyl thiocarbonate are formed.

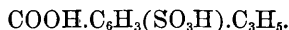
P. P. B.

Introduction of the Hydroxyl Group by Direct Oxidation. By R. MEYER and A. BAUR (*Ber.*, **13**, 1495—1500).—In continuing their investigations (*Ber.*, **11**, 1283, 1787, 1790, 2172; and **12**, 1071, 2238), the authors have submitted the potassium cymenesulphonate

(cymene from camphor) to the action of potassium permanganate. In this way *potassium hydroxypropylsulphobenzoate* is formed, thus:—



The *potassium salt*, $\text{C}_{10}\text{H}_{10}\text{SO}_6\text{K}_2 + 2\text{H}_2\text{O}$, crystallises from absolute alcohol in beautiful shining needles, but is deposited in rhombic tables on slow evaporation of the alcoholic solution; and from its aqueous solution in large rhombic crystals. By evaporation with hydrochloric acid, the potassium salt is converted into an acid which combines directly with bromine, and probably has the formula



That the hydroxypropylsulphobenzoic acid does not contain the hydroxyl in the "nucleus" is shown by its solution yielding no coloration with ferric chloride. The introduction of a hydroxyl group in this cymene is contrary to the experience that such action takes place only in presence of the tertiary group (CH). The author thinks this is explained by the inter-molecular changes which have often been observed in cymene derivatives, a change resulting in the conversion of normal propyl into isopropyl. This oxidation of the methyl group is similar to what takes place in the animal organism (Gerichten, *Ber.*, **11**, 369), and also to the oxidation of chlorocymene (Claus and Wimmel, *Ber.*, **13**, 902), and dibromocymene.

Cymenesulphonic acid when oxidised by nitric acid yields paratolylsulphonic acid, $\text{C}_6\text{H}_3\text{Me}(\text{SO}_3\text{H}).\text{COOH} + 2\text{H}_2\text{O}$, crystallising in needles, which are not hygroscopic. The results from the study of the salts of this acid agree with those of Fischli (*Ber.*, **12**, 615), save that the authors find the following formulæ for the barium and lead salts, viz., $\text{C}_8\text{H}_6\text{SO}_5\text{Ba} + 4\text{H}_2\text{O}$ and $\text{C}_8\text{H}_6\text{SO}_5\text{Pb} + 3\frac{1}{2}\text{H}_2\text{O}$. The melting point of the amide was found to be 218° .

Oxidation of cinnamic acid by potassium permanganate yields chiefly benzaldehyde and benzoic acid, whilst mandelic acid yields benzoylformic acid, $\text{C}_6\text{H}_5.\text{CO}.\text{COOH}$. Hunaeus and Zincke (*Ber.*, **10**, 1489) obtained the same result by oxidising mandelic acid with nitric acid.

P. P. B.

A Fourth Mononitrophenol. By F. FITTICA (*Ber.*, **13**, 711—715).—Liquid mononitrophenol is best prepared by slowly dropping strong sulphuric acid into a mixture of phenol, 10 grams; alcohol, 10; ether, 10; and 8 grams of nitric acid (sp. gr. 1.4). As soon as the liquid begins to boil, it is poured into water. A current of air is blown through the layer of liquid floating on the water, in order to expel the ether, and the heavy oil which separates out is well washed with water and distilled in a current of steam. Ether first passes over, and then an oily liquid, the greater portion of which solidifies after being in contact with calcium chloride for some days. The fraction which still remains liquid consists of a mixture of orthonitrophenol and the new nitro-phenol. The orthonitrophenol is partly removed by distillation in steam; the portion which does not solidify is dissolved in dilute soda, and the sparingly soluble orthonitrophenol salt separated from the new nitrophenate by crystallisation. The

fourth mononitrophenol is liquid at the ordinary temperature, but it solidifies at 0° to a pale yellow crystalline mass (m. p. 34°). It yields an amidophenol crystallising in needles (m. p. 150°), which dissolve readily in water. W. C. W.

New Nitrophenols. By F. FITTICA (*Ber.*, **13**, 1535—1538).—The boiling point of the fourth nitrophenol, already described by the author (preceding abstract), cannot be determined, as it is changed at this temperature into orthonitrophenol. By reducing the compound of nitrophenol and phenol (*loc. cit.*) with tin and hydrochloric acid, or by reducing the fourth nitrophenol under special conditions with tin and hydrochloric acid, a fourth amidophenol is obtained. It crystallises from alcohol in needles (m. p. 151°). The hydrochloride of this amidophenol crystallises in greyish-white needles, which sublime at 230° with partial decomposition. The sulphate is a white powder, consisting of small crystalline needles, soluble in water.

A fifth nitrophenol is obtained by treating the tarry residue obtained after separation of orthonitrophenol from the para-compound with soda. By this means a solid sodium salt is obtained, which is pressed and treated with acid, and the oil obtained submitted to the action of alkali and acid again. The oil obtained solidifies partially, and by crystallisation from ether the new nitrophenol is obtained in yellow needles (m. p. 105 — 106°). It yields an amidophenol, melting at 150° .

In concluding, the author replies to the criticism of Claus (*Ber.*, **13**, 891) on the author's former communication (*loc. cit.*).

P. P. B.

Action of Bromine on Benzyl Cyanide and on Phenylacetic Acid at High Temperatures. By C. L. REIMER (*Ber.*, **13**, 742—748).—*Dicyanostilbene*, $\text{CN} \cdot \text{PhC} : \text{CPh} \cdot \text{CN}$, is formed, together with a small quantity of benzoic acid, when bromine is allowed to drop slowly into a flask containing benzyl cyanide at a temperature of 170° . The product, after purification by washing with water, and solution in a mixture of alcohol and chloroform, is moistened with ether, and pressed between bibulous paper to remove resinous impurities. The solution of the residue in warm benzene deposits on cooling glistening crystalline plates (m. p. 158°), which are soluble in chloroform, benzene, carbon bisulphide, glacial acetic acid, and in hot alcohol. *Dicyanostilbene* is decomposed by alcoholic potash, with evolution of ammonia. If hydrochloric acid is added to the solution after the alcohol has been expelled by boiling, *diphenylfumaric anhydride*, $\text{PhC} : \text{CPh}$

$\text{OC} \cdot \text{O} \cdot \text{CO}$, is precipitated. This substance is deposited from alcohol in pale yellow needles, and from carbon bisulphide in prisms. It melts at 155° , and sublimes without decomposition. The free acid corresponding to the anhydride cannot be isolated, but several of its salts have been prepared. The potassium salt forms colourless needles, which dissolve freely in water; the barium salt is crystalline, and sparingly soluble. Neutral silver diphenylfumarate, $\text{C}_{16}\text{H}_{10}\text{Ag}_2\text{O}_4$, is

amorphous; the acid salt, $C_{16}H_{11}AgO_4$, is crystalline. Both are very sparingly soluble.

Ethyl diphenylfumarate crystallises in prisms (m. p. 54°), which dissolve freely in chloroform and carbon bisulphide.

By the action of ammonia on diphenylfumaric anhydride at 180° , *diphenylfumarimide*, $C_{16}H_{10}O_2.NH_2$, is obtained in yellow needle-shaped crystals, insoluble in water, but soluble in alcohol. This substance melts at 213° , and sublimes without decomposition at a higher temperature. On reduction with zinc and hydrochloric acid, dicyano-stilbene yields a crystalline compound (m. p. 208°), having the composition $C_{16}H_{14}N_2$.

Diphenylfumaric anhydride and benzoic acid are also produced when the product of the action of bromine on phenylacetic acid at 230° is treated with alcoholic potash. W. C. W.

Action of Ethyl Chlorocarbonate on Phenols. By G. BENDER (*Ber.*, 13, 696—703).—The author has examined the products of the action of ethyl chlorocarbonate on potassium salts of the different phenols.

Under these conditions quinol yields diethylic phenyldioxy carbonate, $C_6H_4(O.CO.OEt)_2$. This compound is deposited from an alcoholic solution in colourless needles (m. p. 101°), soluble in ether, but insoluble in water.

Resorcinol.—When ethyl chlorocarbonate acts on resorcinol, carbonic oxide escapes, and mono- and diethyl-resorcinol are formed.

Catechol (pyrocatechin) gives a crystalline compound (m. p. 118°), having the composition $C_7H_4O_3$, which yields diorthotolylcarbamide when boiled with orthotoluidine.

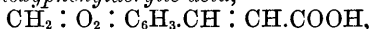
From pyrogallol an ethyl salt having the composition $C_6H_3:(O)_3:C.OEt$ is obtained. This substance melts at 105° , and distils between 250° and 280° with partial decomposition. It is deposited from an alcoholic solution in pearly scales. Ortho-, meta-, and para-cresol yield three liquid isomeric ethylic tolylcarbonates, $C_6H_4.MeO.CO.OEt$, which boil respectively at 236° , 246° , and 245° .

From orcinol, the compound $C_{15}H_{12}O_4$ is obtained in yellow needles, which are sparingly soluble in alcohol, and melt with decomposition at 195° .

β -Naphthol yields a white amorphous mass, having the composition $(C_{10}H_7O)_2C(OEt)_2$. It boils at 298 — 301° .

α -Naphthol forms ethyl-naphthol carbonate, $C_{10}H_7O.CO.OEt$, which crystallises in colourless rhombic plates (m. p. 31°). This body is decomposed by boiling; alcohol distils over, carbonic anhydride escapes, and yellow needle-shaped crystals are deposited (m. p. 240°), of the composition $(C_{10}H_6)_2CO_2$. W. C. W.

Methylenecaffeic and Methylenhomocaffeic Acids and their Derivatives. By C. LORENZ (*Ber.*, 13, 756—761).—*Methylenecaffeic acid* or *Methylenedioxyphenylacrylic acid*,



is prepared by boiling a mixture of piperonal, sodium acetate, and acetic anhydride for six hours in a flask fitted with an upright con-

denser. The aqueous solution of the product is extracted with ether, and the ethereal extract treated with soda. On the addition of hydrochloric acid to the sodium salt, the methylenecaffeic acid (m. p. 232°) is precipitated. It is insoluble in water, but dissolves freely in alcohol and ether. The copper, lead, and zinc salts of this acid are sparingly soluble in water. On reduction with sodium amalgam, the acid takes up 2 atoms of hydrogen, forming methylenehydrocaffeic or methylenedioxyphenylpropionic acid, $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3(\text{CH}_2)_2\text{COOH}$, which crystallises in colourless needles (m. p. 84°). The lead and zinc salts which form needle-shaped crystals, and the silver salt which crystallises in glistening scales, are sparingly soluble in water.

Methylene- α -homocaffeic or *methylenedioxyphenylmethacrylic acid*, $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3\text{CH} : \text{CMe.COOH}$, obtained by the action of sodium acetate and propionic anhydride on piperonal, is deposited from dilute alcohol in colourless prisms (m. p. 193°), soluble in alcohol and ether. The copper and lead salts of this acid are insoluble in water, the zinc salt is sparingly soluble.

By the action of water and sodium amalgam, this acid is converted into *methylene- α -homohydrocaffeic* or *methylenedioxyphenylisobutyric acid*, $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3\text{CH}_2\text{CHMe.COOH}$, which crystallises in prisms (m. p. 77°) of a yellow colour. It is soluble in alcohol and ether. Methylenecaffeic and methylene- α -homocaffeic acids occupy an intermediate position between piperonylic acid, $\text{C}_6\text{H}_4\text{O}_4$, and hydropiperic acid, $\text{C}_{12}\text{H}_{12}\text{O}_4$.
W. C. W.

Nitrometaxylenesulphonic Acid. By W. HARMSSEN (*Ber.*, **13**, 1558—1568).—*Paranitrometaxylene*, $\text{C}_6\text{H}_3\text{Me.Me.NO}_2$ [1 . 3 . 4], is obtained by nitrating metaxylene; it is a liquid which boils at 243 — 244° (corr.), and remains liquid at -20° . Its constitution was shown to be the above by converting it into a xylidine, which yields Jacobsen's metaxylenol, $\text{C}_6\text{H}_3\text{Me.Me.OH}$ [1 . 3 . 4], by means of the diazo-reaction.

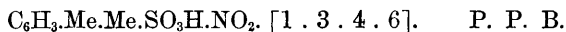
Nitroxylenesulphonic acid, $\text{C}_6\text{H}_2(\text{Me})_2(\text{NO}_2).\text{SO}_3\text{H}$, was obtained by heating the above nitro-derivative with sulphuric acid and converting the product into calcium salt, which gave the free acid when decomposed by sulphuric acid. It crystallises from water in small hygroscopic needles, and from dilute nitric acid in long colourless needles (m. p. 122°).

The calcium salt, $[\text{C}_6\text{H}_2\text{Me}_2(\text{NO}_2).\text{SO}_3]_2\text{Ca} + 6\text{H}_2\text{O}$, crystallises in slender pale-yellow prisms, having a vitreous lustre; it effloresces on exposure to the air; at 18.5° it dissolves in 16 parts of water.

The magnesium salt, $[\text{C}_6\text{H}_2\text{Me}_2(\text{NO}_2).\text{SO}_3]_2\text{Mg} + 9\text{H}_2\text{O}$, forms octagonal plates, which are sparingly soluble in water.

The sodium salt, $\text{C}_6\text{H}_2\text{Me}_2(\text{NO}_2).\text{SO}_3\text{Na} + \text{H}_2\text{O}$, crystallises in shining needles.

The same acid is obtained by nitrating α -metaxylene sulphonic acid, the constitution of which is $\text{C}_6\text{H}_3\text{Me.Me.SO}_3\text{H}$ [1 . 3 . 4]; therefore the constitution of the nitrometaxylenesulphonic acid is—



α -Isophthalosulphonic Acid. By O. JACOBSEN and H. LÖNNIES (*Ber.*, **13**, 1556—1558).—When sodium α -metaxylenesulphonate is oxidised by potassium permanganate and the manganese dioxide removed by treatment with hydrochloric acid it yields an *acid potassium α -isophthalosulphonate*, $C_6H_3(COO)_2(SO_3)H_2K + 2H_2O$. It crystallises in colourless brittle needles, having a vitreous lustre, and is sparingly soluble in cold water.

α -Isophthalosulphonic acid, $C_6H_3(COOH)_2.SO_3H + H_2O$, is obtained by decomposing the insoluble lead salt with sulphuretted hydrogen; it crystallises in colourless flat needles. It resembles the γ -isophthalosulphonic acid (*Ber.*, **13**, 704), and is more easily crystallised from sulphuric acid than from water. Fused with potash, it yields α -hydroxyisophthalic acid. It melts between 235—240°, and is more easily soluble in water than the anhydrosulphonamine-isophthalic acid.

Barium isophthalosulphonate, $C_6H_3(COO)_2(SO_3)HBa + 3H_2O$, is obtained as a white crystalline precipitate by adding barium chloride to the solution of the free acid or its acid potassium salt. Barium chloride produces a precipitate only after some time in a solution of the acid in ammonia; under the same conditions sulphonamineisophthalic acid gives a precipitate also, the anhydro-acid does not, however, give a precipitate with barium chloride.

Isophthalosulphonic and anhydrosulphonamine-isophthalic acids behave differently with silver nitrate. In the case of the former, neither the free acid nor its potassium salt gives a precipitate with silver nitrate, whilst the latter, either as free acid or potassium salt, gives a voluminous precipitate, which becomes crystalline on standing.

P. P. B.

γ -Isophthalosulphonic Acid and γ -Hydroxyisophthalic Acid. By H. LÖNNIES (*Ber.*, **13**, 703—707).— *γ -Isophthalosulphonic acid*, $C_6H_3(SO_3H)(COOH)_2$ [1 : 3 : 5], is prepared by heating isophthalic acid with fuming sulphuric acid at 200° for six hours. The liquid is then diluted with twice its volume of water which precipitates the unaltered isophthalic acid: the sulphonic acid is deposited as a crystalline mass on cooling. The sulphonic acid is deposited from dilute sulphuric acid in colourless prisms containing 2 mols. H_2O . The crystals are deliquescent at the ordinary temperature, but begin to effloresce at 60°. The anhydrous acid melts at 257° with decomposition.

The barium salt, $[C_6H_3(SO_3)(COO)]_2Ba_3 + 8H_2O$, crystallising in silky needles, and the calcium salt crystallising in transparent prisms, are freely soluble in water. A solution of the sodium salt yields precipitates with mercuric nitrate, ferric chloride, copper acetate, and lead acetate.

The preparation and properties of γ -hydroxyisophthalic acid have been described by Heine (*Ber.*, **13**, 491). The anhydrous acid melts at 288°, and requires 3,280 times its weight of water at 5° for complete solution. A solution of the potassium salt is precipitated by ferric chloride, barium chloride, copper sulphate, silver nitrate, and lead acetate. Zinc sulphate does not yield an immediate precipitate, but after some time small prismatic crystals are deposited which are sparingly soluble in water.

W. C. W.

Anhydrosulphonamine-isophthalic Acid. By O. JACOBSEN (*Ber.*, **13**, 1554—1555).—A further examination of the body formed by the oxidation of sulphonamine-metatoluic acid, has confirmed the views of Remsen (this Journal, **38**, 258), viz., that anhydrosulphonamine-isophthalic acid is obtained.
P. P. B.

Amarine and Lophine. By E. FISCHER and H. TROSCHE (*Ber.*, **13**, 706—711).—Amarine dichromate, $(C_{21}H_{16}N_2)_2H_2Cr_2O_7$, is thrown down as a yellow precipitate when chromic acid is added to a solution of amarine in dilute acetic acid. The solution of this salt in glacial acetic acid is converted into *lophine* by boiling. A solution of lophine in glacial acetic acid is oxidised by chromic acid at 100° with the formation of benzamide and dibenzamide.

Lophine dissolves in strong sulphuric acid at 170° , forming a disulphonic acid, which is sparingly soluble in water and alcohol. It is not attacked by strong hydrochloric acid, but is reduced to lophine by sodium-amalgam.

The mono-sodium salt, $C_{21}H_{14}N_2(SO_3)_2NaH + 2H_2O$, crystallises in white needles, sparingly soluble in alcohol and in water.

An unstable crystalline compound, $C_{21}H_{16}N_2Br_8 \cdot HBr$, is produced by the action of bromine on lophine hydrobromide.

The authors believe that amarine and lophine contain the group

$$\begin{array}{c} C_6H_5-C \cdot N \\ | \\ C_6H_5-C \cdot N \end{array} \begin{array}{l} \\ \\ \end{array} \begin{array}{l} \\ \\ \end{array} C_6H_5.$$
The formula for lophine, $C_{21}H_{16}N_2$, was confirmed by the vapour-density determination.
W. C. W.

Indoline. By E. GIRAUD (*Compt. rend.*, **90**, 1429—1430).—Flavindin dissolved in dilute soda is treated with sodium-amalgam (3 per cent.), when a dirty yellow powder is precipitated; this is washed, dissolved in alcohol, and the solution diluted with water, when the indoline is precipitated, and may be purified by sublimation. It is probably formed according to the equation, $C_{32}H_{24}N_4O_5 + 14H = 2(C_{16}H_{14}N_2) + 5H_2O$. It gives the same reaction with picric acid as the indoline described by Schützenberger. When dissolved in chloroform and treated with chlorine, it yields a chlorinated derivative, $C_{16}H_{12}N_2Cl_2$. An orange-yellow dinitro-compound, $C_{16}H_{12}N_2(NO_2)_2$, is obtained by treating indoline with nitric acid; it is soluble in alcohol, but insoluble in water. By treating indoline with fuming sulphuric acid at 180° , and saturating the product with sodium carbonate, $C_{16}H_{12}N_2(SO_3Na)_2$ is obtained.
L. T. O'S.

Derivatives of Anthraquinonesulphonic Acid. By D. A. McHOUL (*Ber.*, **13**, 692—694).—*Anthraquinonesulphonic chloride*, $C_{14}H_7O_2 \cdot SO_2Cl$, is prepared by heating equivalent quantities of anthraquinonesulphonic acid and phosphorus pentachloride at 180° for four hours. The residue which remains after the phosphorus oxychloride is distilled off is extracted with hot water and recrystallised from boiling benzene. The chloride crystallises in pale-yellow plates (m. p. 193°) which dissolve in benzene, toluene, and glacial acetic acid. By the action of water at 160° , it is converted into anthraquinonesulphonic acid.

Anthraquinonesulphamide, $C_{14}H_7O_2.SO_2NH_2$, formed by heating the sulphonic chloride with alcoholic ammonia at 140° , is deposited from a solution in glacial acetic acid in long yellow crystals (m. p. 261°) which are insoluble in alcohol, toluene, chloroform, and carbon bisulphide.

Anthraquinonesulphanilide, $C_{14}H_7O_2.NHPh$, obtained by heating the sulphonic chloride with a solution of aniline in toluene at 180° , forms long brown prisms (m. p. 193°) soluble in alcohol and glacial acetic acid.

Anthraquinonedimethylamidophenylsulphone, $C_{14}H_7O_2.SO_2C_6H_4.NMe_2$ (m. p. 171°), is obtained by the process described by Michler and Salathe (*Ber.*, **12**, 1789; this Journal, **38**, 108) for preparing α -naphthyl dimethylamidophenylsulphone.

The reduction of the sulphonic chloride by sodium-amalgam yields sodium anthracenesulphonate, sodium anthracenehydridesulphonate, and a small quantity of anthraquinone. W. C. W.

Gum Resin from Arizona and California. By J. M. STILLMANN (*Ber.*, **13**, 754—756).—The resinous substance found on the twigs of the *Larrea Mexicana* and *Acacia greggii* in Arizona and California, appears to be identical with Indian shellac. It is composed of resin, &c., soluble in alcohol, 61.7; colouring matter soluble in water, 1.4; soluble in soda, 26.3; insoluble residue, 6.0; colouring matter soluble in soda and loss, 4.6 per cent. W. C. W.

A Substance Extracted from *Thalictrum Macrocarpum*. By M. HANRIOT and E. DOASSANS (*Bull. Soc. Chim.* [2], **34**, 83—84).—In a former communication the authors described a yellow crystalline substance from the *Thalictrum macrocarpum*, which was named by them "thalictrin." They propose to change the name to *macrocarpin*. In order to obtain this substance, the roots of the thalictrum are exhausted with alcohol, the excess of which is distilled off in a vacuum; it is then purified from a resin by ether, and finally precipitated with distilled water. Macrocarpin is a yellow substance, crystallising in needles, soluble in water and alcohol, but insoluble in ether; its best solvent is amyl alcohol. It is neutral, precipitated by acids, but soluble in ammonia. The analyses gave: C = 58.25; H = 5.67; O = 86.08. Owing to the small quantity at the authors' disposal, they were unable to study the products of decomposition and assign a formula. V. H. V.

Thalictrine. By E. DOASSANS (*Bull. Soc. Chim.* [2], **34**, 84).—By exhausting crude macrocarpin with ether, an alkaloid, thalictrine, is obtained; a colourless crystalline substance, insoluble in cold and warm water, soluble in ether and in alcohol. With hydrogen nitrate, it gives crystals of thalictrine nitrate. In its properties and reactions it resembles most nearly aconitine. V. H. V.

Catechin. By C. LIEBERMANN and TAUCHERT (*Ber.*, **13**, 694—696). The catechin used in these experiments was prepared from catechu by Loewe's process (*Zeits. Anal. Chem.*, 1874, 113), but it was recrystal-

lised twice from hot water before it was treated with ethyl acetate. It is deposited from an aqueous solution in minute needle-shaped crystals, having the composition $C_{21}H_{20}O_9 + 5H_2O$. *Diacetic catechin*, $C_{21}H_{18}\bar{A}c_2O_9$, obtained by the action of acetic anhydride and sodium acetate on catechin, crystallises in yellow needles and prisms (m. p. 130°), which are insoluble in water and ligroin, but dissolve freely in other solvents.

Dichloroacetic catechin, $C_{21}H_{16}Cl_2\bar{A}c_2O_9$ (m. p. 169°), is prepared by passing chlorine through a concentrated solution of diacetic catechin in glacial acetic acid: the substance is precipitated on the addition of water. It is soluble in alcohol and ethyl acetate. *Monobromoacetic catechin*, $C_{21}H_{17}Br\bar{A}c_2O_9$, is deposited from an alcoholic solution in white needles (m. p. 120°).

The existence of these compounds shows that catechin has the composition $C_{21}H_{20}O_9$.
W. C. W.

Alkannin. By G. CARNELUTTI and R. NASINI (*Ber.*, **13**, 1514—1516).—This body was obtained by extracting commercial colouring matter with dilute potash solution; this extract was shaken with ether to remove a reddish-brown acid, an impurity present in the alkannin obtained by Pelletier, Bolley, and Weydler. The solution in potash when saturated with carbonic anhydride gives a precipitate of alkannin, which was further purified by solution in ether. It is obtained as a dark reddish-brown mass, with metallic lustre, and is sparingly soluble in the ordinary solvents; it is most easily soluble in chloroform and glacial acetic acid. Its alcoholic solution is not changed by exposure to light or by continued boiling. The analytical results show its formula to be $C_{15}H_{14}O_4$, whilst Pelletier obtained $C_{17}H_{10}O_4$, and Bolley and Weydler $C_{35}H_{20}O_8$ from their analyses.

Acetic and benzoic chlorides have no action on alkannin; a diacetyl derivative, $C_{15}H_{12}O_4\bar{A}c_2$, is obtained by heating it with acetic anhydride and sodium acetate: it is a brown powder which crystallises from glacial acetic acid in dirty yellow crystalline grains.

A barium salt containing 2 atoms of barium to 3 molecules of alkannin is obtained by precipitating the alcoholic solution with ammoniacal barium chloride.

Nitric acid or bromine in alkaline solution oxidises alkannin to oxalic and succinic acids. Bromine acts on solid alkannin, but not on its solutions.

Alkannin appears to be related to santalin.

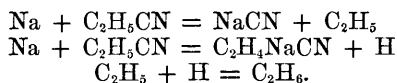
P. P. B.

Derivatives of Santonin. By S. CANNIZZARO and J. CARNELUTTI (*Ber.*, **13**, 1516—1517).—By the fusion of santonous and isosantonous acids with barium hydrate (*Ber.*, **12**, 1574) the authors obtained a body having the formula $C_{12}H_{12}O$. Since this body when distilled with zinc-dust yields a hydrocarbon, $C_{12}H_{12}$, whose physical properties, and the properties of its picric acid compound, and of its tribromoderivative, show it to be dimethylnaphthalene, the authors conclude that the compound $C_{12}H_{12}O$ is dimethylnaphthol. The dimethylnaphthalene contains the methyl groups in the same relative position that the bromine atoms occupy in Glaser's dibromonaphthalene (m. p. $80.5-81^\circ$).

Santonous acid distilled over zinc-dust yields some dimethylnaphthol, also dimethylnaphthalene and propylene. A small quantity of xylene appears to be formed.
P. P. B.

Cyanethine, and New Bases derived from it. By E. v. MEYER (*J. pr. Chem.* [2], 22, 261—288).—Cyanethine was discovered 33 years ago by Kolbe and Frankland (*Annalen*, 65, 269), and its homologue cyanmethine has been since described by Bayer (this Journal, 1871, 397).

Cyanethine is prepared by acting on tolerably large pieces of clean sodium with ethyl cyanide in a retort provided with an upright condenser, the upper end of which is air-tight, and has a bent glass tube fitted to it which dips into mercury. The apparatus is filled with carbonic anhydride; one-third of the ethyl cyanide is added at first, and the rest gradually as the reaction becomes less violent. The excess of cyanide is removed by distillation, and the yellow-coloured product powdered and washed with water. It is then dried on porous plates and crystallised from alcohol (of 90 per cent.). The chief processes of the reaction are shown by the following equations:—



Cyanethine melts at 189°. One part dissolves in 1,365 to 1,380 parts of water at 17°, but it is tolerably soluble in alcohol.

A concentrated solution of cyanethine in hydrochloric acid crystallises in large transparent striated prisms, which, when dried over quicklime and sulphuric acid, contain about 1 mol. of water. These crystals dried at 110°, have the composition $\text{C}_9\text{H}_{15}\text{N}_3 \cdot \text{HCl}$.

Cyanethine forms a double salt, $(\text{C}_9\text{H}_{15}\text{N}_3)_2 \cdot \text{AgNO}_3$, with silver nitrate. It is also shown by the action of ethyl iodide to belong to the tertiary bases. Nitrous acid has no marked action on it, but it is oxidised by permanganate with formation of formic acid as the chief product; carbonic anhydride is evolved at the same time, while an ammonium salt is found in the solution together with a second acid, probably propionic.

When cyanethine is heated with tolerably concentrated mineral acid, it yields a monacid base containing oxygen, $\text{C}_9\text{H}_{14}\text{ON}_2$. This base crystallises from hot water in fine tufts of brilliant needles: from alcohol in long striated prisms; when precipitated by ammonia from one of its salts, it forms intricate, sometimes dendritic, acicular masses; carefully heated, it sublimes in small needles far below its melting point, which lies between 156° and 157°. One part of this base requires 133 parts of water for solution, but it does not impart any alkaline reaction to the water. It is most soluble in chloroform and benzene. The salts are soluble in water, to which they give an acid reaction, and for the most part crystallise well.

The *hydrochloride*, $\text{C}_9\text{H}_{14}\text{ON}_2 \cdot \text{HCl}$, is obtained by evaporation of the hydrochloric acid solution and drying at 110° as a white flocculent crystalline powder, small quantities of which sublime in minute prisms.

The *platinochloride*, $(C_9H_{14}ON_2.HCl)_2.PtCl_4$, forms yellow rhombic plates which dissolve easily in water, but sparingly in alcohol.

The *nitrate*, $C_9H_{14}ON_2.HNO_3$, crystallises in fine (probably monoclinic) prisms which undergo decomposition at 100° . The *acid oxalate*, $C_9H_{14}ON_2.C_2O_4H_2$, is anhydrous.

The body which has acted as a base in the above salts can also exchange an atom of hydrogen for one of silver. The *silver salt*, $C_9H_{13}AgON_2$, is precipitated as a white, bulky, microscopic crystalline powder which is readily soluble in ammonia and in dilute nitric acid. Similar compounds could not, however, be obtained with copper, lead, &c. The ready solubility of the base, $C_9H_{14}ON_2$, in alkalis, seems to indicate that it forms compounds with them, but it is separated from them again by carbonic anhydride. The reaction with ethyl iodide shows that it belongs to the tertiary bases. It unites with acetic chloride to form the compound $C_9H_{14}ON_2.CH_3COCl$. As this base is not altered by heating with acetic anhydride at 180° , the oxygen would seem to be united with hydrogen as hydroxyl. Heating with excess of hydriodic acid at 200° decomposes a small part of the base with formation of ammonia and probably propionic acid.

Potassium permanganate in acid solution oxidises it, the nitrogen being evolved in the form of ammonia; in alkaline solutions propionic acid (and probably a little acetic acid) is also formed. When treated with phosphorus pentachloride, a new base is produced of the formula $C_9H_{13}ClN_2$. This base is a bright yellow oil with an unpleasant odour, and cannot be distilled at the ordinary pressure without decomposition. It is insoluble in water. On heating with ammonia and alcohol, cyanethine is re-formed, which shows that cyanethine contains a molecule of amidogen. When alcoholic potash acts on the compound $C_9H_{13}ClN_2$ a new base, $C_9H_{13}(OEt)N_2$, is formed; it is a faintly-coloured oil with a cabbage-like smell. It can be distilled without change at 229° to 231° . Strong hydrochloric acid converts it into the base $C_9H_{14}ON_2$ or $C_9H_{13}(OH)N_2$. When the base $C_9H_{14}ClN_2$ is acted on by zinc and hydrochloric acid a double zinc salt, $(C_9H_{14}N_2.HCl)_2.ZnCl_2$, is formed, but it is not improbable that this salt contains also an analogous base, $C_9H_{16}N_2$.

On continued agitation, the base, $C_9H_{14}N_2$, dissolves in water in considerable quantities, and imparts to it an alkaline reaction; when the solution is heated, the base separates in oily drops. It is a clear liquid with high refractive power and an unpleasant narcotic smell; when the vapour is inhaled, it produces a heavy feeling in the head, so that great care is necessary in working with it. It boils at $204-205^\circ$, and is easily volatilised in steam. It does not reduce Fehling's solution; an ammoniacal solution of a silver salt is only reduced on continued heating. Powerful oxidising agents such as chromic acid, &c., act energetically on it. Crystalline salts of the base have not been obtained. The above properties of the base strongly resemble those of conine, and its physiological action is similar, but more violent than that of conine. It may perhaps be cyanoconine for $C_8H_{14}(CN)N = C_9H_{14}N_2$. If this is the case, the bases described in the paper may be expressed as follows:—

$C_8H_{14}N_2 = C_8H_{14}(CN)N$, cyanoconine.

$C_8H_{13}ClN_2 = C_8H_{13}Cl(CN)N$, chlorocyanoconine.

$C_8H_{13}(OH)N_2 = C_8H_{13}(OH)(CN)N$, oxycyanoconine.

$C_8H_{13}(OC_2H_5)N_2 = C_8H_{13}(OC_2H_5)(CN)N$, oxyethylcyanoconine.

$C_8H_{13}(NH_2)N_2 = C_8H_{13}(NH_2)(CN)N$, amidocyanoconine =
cyanethine. G. T. A.

Bases of the Pyridine Series. By O. DE CONINCK (*Compt. rend.*, 91, 296—297).—The bases of this series formed in the distillation of cinchonine with potash have been separated and purified by the author. They are isomeric with the bases of the same name found in coal-tar naphtha, and in Dippel's oil. After separating them as far as possible by fractional distillation, the different fractions are treated with excess of hydrochloric acid, agitated two or three times with ether, the ether separated, and excess of potash solution added. The separated bases are taken up by ether; the ethereal solution dried over potash and distilled.

Lutidine, C_7H_9N , is a colourless, mobile, strongly refracting liquid, with peculiar odour and burning taste. It is very hygroscopic, and almost insoluble in water. Boiling point, 135° ; vapour-density, 3.8 (found); 3.71 (calculated); sp. gr. at 0° , 0.9593.

Lutidine hydrochloride, $C_7H_9N.HCl$, forms white, deliquescent, lamellar crystals. The hydrobromide is similar. The platinochloride crystallises in fine orange-red needles; treated with boiling water, it loses 2 mols. HCl , and crystallises in yellow needles. The aurochloride is a shining yellow powder.

Collidine, $C_8H_{11}N$, boils at 195° , and is similar in appearance and properties to lutidine. Vapour-density, 4.25 (found); 4.19 (calculated); sp. gr., 0.9656 at 0° . The platinochloride is an orange-red powder, transformed by boiling water into minute yellow needles.

Parvoline has not yet been obtained quite pure; it boils at about 220° . The platinochloride forms a brownish-yellow powder.

Lutidine from Dippel's oil is of sp. gr. 0.946 and b. p. 155.5° .

Collidine " " " 0.944 " 180.

Parvoline " " " boils at 188.

J. M. H. M.

Crystalline Quinoidine Borate. By J. JOBST (*Ber.*, 750—751).

—The substance described by Pavesi (*la Farmacia*, 1879, 26) as a quinoidine borate is merely a mixture of boric acid and quinoidine, from which the base is completely removed by recrystallisation.

W. C. W.

Hyoscine. By A. LADENBURG (*Ber.*, 13, 1549—1554).—In a former communication (*Ber.*, 13, 910), the author stated, that an alkalioid accompanies hyoscyamine, which is known as "amorphous hyoscyamine." To this the author gives the name hyoscine; it is obtained in commerce as a syrup, from which, by conversion into the aurochloride and recrystallisation of the latter, it may be obtained in a tolerably pure state. When the hyoscine obtained from the aurochloride is decomposed by baryta, it yields tropic acid and a base isomeric with tropine, which is styled pseudotropine.

Pseudotropine forms a white crystalline mass; it boils at 241—243° (tropine boils at 229°). Its *platinochloride* $(C_8H_{15}NOHCl)_2.PtCl_4$, has been obtained in well-defined crystals, belonging to the rhombic system, a complete description of which is given. The *aurochloride*, $C_8H_5NO.HCl.AuCl_3$, has a solubility similar to that of tropine aurochloride; the appearance of the crystals is, however, different. The *picrate* and *double salt with mercuric chloride* have been obtained in well-defined crystals.

The aurochloride of hyoscyine may be obtained pure by first boiling hyoscyine hydrochloride with animal charcoal. The aurochloride prepared from the hydrochloride so purified crystallises well, and melts at 198°.

The reactions of hyoscyine are similar to those of hyoscyamine. Potassio-mercuric iodide gives a light yellow amorphous precipitate, with acid solution of hyoscyine, and mercuric chloride, an amorphous precipitate; in some cases an oil is obtained. Iodine solution gives a black oily periodide, and potassium ferrocyanide a white amorphous precipitate.

The physiological action of hyoscyine resembles that of atropine.

Atropine, hyoscyamine, and hyoscyine are isomerides, whilst homatropine is a homologue containing CH_2 less than these alkaloids.

P. P. B.

Ptomaines considered in Relation to Judicial Chemistry and Toxicology. By T. HUSEMANN (*Arch. Pharm.* [3], 16, 169—181).—The name “ptomaines” has been given by Selmi to bodies which have been detected in exhumed corpses, and resemble the vegetable alkaloids in their chemical reactions and physiological effects. The author gives a summary of the observations already published on this class of bodies, and considers the very important bearing they have on the study of poisons and on forensic medicine. It becomes extremely important to discover, if possible, reactions which will distinguish between these poisonous bodies, which are the result of putrefactive processes, and those very similar vegetable principles which, when administered, may produce death. Bodies of the “ptomaine” class seem to have different physiological actions. Some appear to act as poisons, others are inactive: whilst others again counteract the effects of poisonous substances.

The study of these bodies embraces also the poisonous effects produced by food in certain conditions of putrefaction or fermentation. Panum showed that albuminous substances by putrefaction yielded a poisonous body, acting like a ferment, soluble in water, insoluble in alcohol, and capable of withstanding a temperature of 100°. This has been confirmed by Bergmann, who describes a compound called sepsin, generated by putrefaction.

It appears from the researches of Panum and of Schweninger, that compounds having different physiological actions are produced at different stages of decay.

Sonnenschein and Zuelzer found in an anatomical maceration fluid an alkaloid which resembled atropine in its action, and poisonous sausages produced a similar effect; the existence of a product of decay which caused tetanic symptoms was also noticed. Aebi and

Schwazenbach detected a compound allied to an ethereal salt in extract from dead bodies. Substances derived from putrefaction of maize certainly produce tetanic symptoms, as was first proved by Lombroso and Erba; and this action has been traced to the presence of basic substances. It appears probable, however, that drowsiness, loss of sensation, and weakening of the action of the heart may be due to the presence of acid bodies in the extract of putrefied maize, since lactic acid and sodium lactate produce effects similar to those of morphine. Lombroso thinks that the tetanic and narcotic action of extract of putrefied maize, and its beneficial effect on several skin affections, indicate the possible origin of pellagra in diseased or putrid maize. This would explain the prevalence of pellagra in the South European maize-growing countries, and in other countries it may originate from the putrefaction of albuminoid substances of other cereals. This kind of putrefaction cannot be caused by artificial heat, although it occurs only in hot summer weather, and probably therefore requires the presence of special microscopic organisms. A similar explanation may be applied to tetanic symptoms caused by wounds and prevented by the Lister treatment. Frequently the tetanising principle in the maize extract has its action marked by a narcotic substance; just as Ranke showed that the physiological action of strychnine in bodies long buried may be masked by ptomaines.

Lombroso's suggestion that skin complaints may be due to putrefactive products of maize has its known analogues in erysipelas caused by wound poisoning, and in skin eruptions caused by eating bad fish and other putrefying substances. Such poisonous effects are, however, often produced by parts of living organisms, as for instance by the beard of the mussel; and they are not produced on all individuals, since dogs accustomed to eat decomposing substances are not affected by putrefactive principles.

The relation of these products of putrefaction to certain diseases is evident from the fact, that Sonnenschein's alkaloid is found in the bodies of patients dying from typhus fever, and many individuals poisoned by decomposing food show marked typhus symptoms.

In many cases of poisoning by cheese, it was found that the bad effect was not due to vegetable growths or to microscopic organisms, and the cheese was frequently fresh.

It appears from the study of the literature concerning ptomaines, that they are usually produced in bodies which, after brief exposure, have been excluded from air, as in buried bodies, sausages, and tinned foods; and further, in these cases, the production chiefly occurs in the internal portions. Cases, however, are known where similar principles have been present in comparatively fresh substances which have been constantly exposed to the air: hence under the name "ptomaines" must be included all alkaloidal products of decay, whether formed in the presence or absence of air.

F. C.

Papain. By A. WURTZ (*Compt. rend.*, 90, 1379—1385).—The sap of the *Carica papaya* contains a soluble ferment, which the author and Bouchut have described (this Journal, 1879, Abst., 1048). The ferment is obtained by making incisions in the bark of the tree and in the

unripe fruit, when a milky sap exudes, which coagulates on exposure to the air. By expressing the liquid from the coagulum, and adding alcohol to it, a precipitate of papain is obtained. Papain is also obtained from the coagulum by triturating it with water several times, concentrating the solutions, and adding alcohol. Prepared in this way it differs slightly in composition from that obtained from the liquid portion of the sap. Papain of another composition is also obtained by mixing the sap obtained from the fruit with water to form a pulp, filtering, concentrating the solution, and adding alcohol. By washing the residue and concentrating the filtrate, a further quantity of papain is obtained. It appears, therefore, that the soluble ferment of *Carica papaya* is not of constant composition. All the preparations contain from 4 to 10 per cent. of ash, whilst after deducting the ash the percentage of carbon varies from 46 to 53, and that of nitrogen from 14 to 18; it also contains about 2.2 per cent. of sulphur. Those preparations giving the greatest percentage of carbon were obtained either by dialysing the precipitate obtained with alcohol, or by precipitating adhering albumin, &c., with subacetate of lead, and separating the excess of lead with sulphuretted hydrogen, and precipitating the papain with alcohol. The ferment thus obtained acts energetically on fibrin, and its composition resembles that of the albuminoids. It is very soluble in water, dissolving in less than its own weight like gum. The solution when boiled or allowed to stand for some time becomes turbid, but the papain does not coagulate like albumin. Hydrochloric and nitric acids precipitate papain, but the precipitates are soluble in excess. Orthophosphoric and acetic acids do not give precipitates with papain, but with metaphosphoric acid a precipitate is formed. Subacetate of lead produces a turbidity in papain solutions; on adding potash and boiling, it becomes black. Millon's reagent gives a yellowish-white precipitate, which on boiling becomes brick-red. Papain does not act so energetically on fibrine as the *trypsine* of Kühne.

The author has also obtained a saponifiable fat, and a nitrogenous body from the juice of the *Carica papaya*.

L. T. O'S.

Chemistry of Vegetable Physiology and Agriculture.

Artificial Generation of Spleen-Fungus. By H. BUCHNER (*Bied. Centr.*, 1880, 594—598).—The fungus which causes inflammation of the spleen in animals can be slowly transformed into hay bacteria by continuous cultivation in a solution of extract of meat for some months, and the converse of this change of form may be effected by the growth of hay bacteria in blood. J. K. C.

The Function of Fat in Germination. By A. LADUREAU (*Bied. Centr.*, 1880, 628).—When seeds are brought in contact with water,

decomposition and acidification of the contained fatty matter is produced, whereby heat is evolved and germination is hastened.

J. K. C.

Growth of Sprouts on Potatoes. By K. KRAUS (*Bied. Centr.*, 1880, 602—606).—The sprouts on potatoes flourish in proportion to their nearness to the apex of the tuber. Treatment with water in sunlight increases the growth forty or fifty times, although this is not the case in the dark. For the growth of the young tubers, absence of light is necessary.

J. K. C.

Vegetation of Oil-producing Plants. By MAQUENNE (*Bied. Centr.*, 1880, 630).—The formation of highly-reduced oils is not accompanied by a loss of oxygen in the whole plant. In all oil-producing plants there exists an easily oxidisable substance, similar in its properties to tannin.

J. K. C.

Distribution of Sugar in Sorghum. By F. MEUNIER (*Bied. Centr.*, 1880, 629).—The amount of cane-sugar gradually decreases from the lowest part to the summit of the cane, whilst the middle is richest in glucose.

J. K. C.

Pressure in Plant-stems. By J. BÖHM (*Bied. Centr.*, 1880, 629).—This pressure the author attributes to the evolution of gases in the stem, and not to osmotic forces.

J. K. C.

Successful Growth of Flax in Saxony. By OEHME and others (*Bied. Centr.*, 1880, 598—600).—In the case of one field, a profit of 80 per cent. was obtained on the total outlay connected with the culture and cleaning of the flax.

J. K. C.

Cultivation of Beet. By E. WOLLNY (*Bied. Centr.*, 1880, 606—613).—The author shows that a certain amount of room, varying with the sort of plant, is necessary to obtain the maximum yield. With regard to ridging of the plants, transplanting, &c., the author's results agree with those of former investigators.

J. K. C.

Experiments with Various Kinds of Beet. By C. BRIER and L. JEHLE (*Bied. Centr.*, 1880, 624—626).—Further experiments are necessary to determine which of the 13 kinds of beet under investigation are best for the soil where the experiments were carried out, as the results were very irregular.

J. K. C.

Cultivation of Beetroot. By A. PAGNOUL (*Bied. Centr.*, 1880, 629).—These researches are merely of local interest.

J. K. C.

Influence of Trenching on the Temperature and Moisture of Soil. By E. WOLLNY (*Bied. Centr.*, 1880, 563—567).—Experiments with five different kinds of soil showed that the temperature was raised in the day and lowered at night by trenching the earth, the mean temperature being, however, greater than on level soil. The amount of moisture was less in the trenches than on the flat. These

observations are explained by the fact that there is a greater surface exposed in the trenches, and consequently radiation is greater at night: also, that the sun's rays fall more perpendicularly on parts of the trenches than on level ground.

J. K. C.

Descent of Rain-water down Tree Stems. By W. RIEGLER (*Bied. Centr.*, 1880, 561—563).—The quantity of rain-water which trickles down the trunks of trees to the earth varies with the upward or downward extension of the branches and the force of the rainfall. In the case of firs, it is much less than in beech and oak.

J. K. C.

Worthlessness of Phosphates as Manure for Certain Soils. By P. P. DEHÉRAIN and MEYER (*Bied. Centr.*, 1880, 567—570).—In the case of a field at Grignon, phosphate, when used as manure, was found to produce no effect, although the soil was not rich in phosphates.

J. K. C.

Curacao Guano. By F. HULWA (*Bied. Centr.*, 1880, 626—627).—This guano is of very uniform quality, containing about 88 per cent. of calcium triphosphate, and is easily soluble in acid.

J. K. C.

Manuring Experiments on Arable Land. By A. SCHUMACHER (*Bied. Centr.*, 1880, 580—582).—The manure used was superphosphate and Chili saltpetre. The results were, however, not successful, as the quantity employed was insufficient.

J. K. C.

Manuring Experiments with Mangold Wurzel and Beet. By H. POGGE-ROGGOW (*Bied. Centr.*, 1880, 572—575).—The mangolds were manured with Chili saltpetre and superphosphate, which in every case more than paid for itself, whereas the 24 experiments with beet were all, with one exception, unsuccessful in a pecuniary point of view.

J. K. C.

Analysis of Pond Slime. By HOLDEFLEISS (*Bied. Centr.*, 1880, 627).—The percentage of nitrogen varied from 0·78 to 0·07; of phosphoric acid, 0·15 to 0·02; of potash, from 0·15 to 0·10; and of lime, from 0·75 to 0·26 in the upper and lower layers of slime.

J. K. C.

Best Method of Manuring Potatoes. By PÄTOW-LALENDORF (*Bied. Centr.*, 1880, 575—577).—The most successful method seems to be to partially dig the manure into the soil.

J. K. C.

Manuring of Beetroot. By A. DUBOUY (*Bied. Centr.*, 1880, 570—571).—The author concludes from his experiments that potash has an injurious action on the amount of sugar in the root; this inference, however, can hardly be considered as established by the results obtained.

J. K. C.

Analytical Chemistry.

Apparatus for the Volumetric Estimation of Nitrogen. By H. SCHWARZ (*Ber.*, 13, 771—773).—This is a convenient modification of Zulkowsky's apparatus for collecting the nitrogen evolved in organic analyses of nitrogenous compounds by Dumas's method.

W. C. W.

Action of Organic Acids on Minerals. By H. C. BOLTON (*Ber.*, 13, 726—734).—The author points out that a large number of minerals are decomposed, either by a hot concentrated solution of citric acid, or by the combined action of citric acid and sodium nitrate, potassium iodide or ammonium fluoride, and he suggests that this acid would, on account of its safe portability, prove a valuable reagent during mineralogical excursions. Tables are given of this reaction with a large number of minerals.

W. C. W.

Estimation of Retrograde Phosphoric Acid. By A. GRUPE and others (*Bied. Centr.*, 1880, 582—584).—The solvent action of ammonium citrate is greater at 35° C. than at the ordinary temperature, and in using this as a reagent for the estimation of retrograde phosphate, care must be taken to first remove by washing soluble salts of magnesia, which have the effect of rendering bicalcium phosphate insoluble in ammonium citrate; the presence of calcium carbonate also has the same effect.

J. K. C.

Retrograde Phosphoric Acid. By M. A. MILLOT (*Bied. Centr.*, 1880, 577—580).—The author finds that when mineral superphosphates contain a considerable quantity of ferric oxide, a part of the phosphoric acid combines with the iron, forming a compound insoluble in ammonium citrate, even when a sufficient quantity of sulphuric acid has been used in the decomposition of the phosphate. Calcium monophosphate also after a time becomes converted into diphosphate, but not into triphosphate. The presence of alumina also gives rise to the formation of phosphates soluble in ammonium citrate. When calcium carbonate is mixed with superphosphate in sufficient quantity, tricalcium phosphate is formed, insoluble in ammonium citrate; if, however, a neutral solution of potassium citrate is employed, instead of ammoniacal potassium citrate, the retrograding of the phosphoric acid appears to be much greater than it really is.

J. K. C.

Alkanet Red, a Test for Magnesium Salts. By F. V. LEPEL (*Ber.*, 13, 763—766).—Alkanet red, the colouring matter obtained from the roots of the false alkanet, *Anchusa tinctoria*, dissolved in a mixture of alcohol (2 parts), and ether (1 part), and diluted with water, exhibits an absorption spectrum composed of three bands. The violet-coloured solution produced by the addition of ammonium carbonate to this mixture, is changed to blue by a minute quantity of a

magnesium salt, and a characteristic fourth absorption band is formed. By this test, 0.05 mgrm. in 1 c.c. of liquid can be detected.

W. C. W.

Vegetable Colouring Matters as Tests for Magnesium Salts.

By F. v. LEPEL (*Ber.*, **13**, 766—768).—Magnesium salts alter the absorption spectra of the colouring matters derived from (1) the roots of *Anchusa tinctoria* and common beet (*Beta vulgaris*); (2) the flowers of the dahlia, dragon's mouth (*Antirrhinum majus*), horse chestnut, hyacinth, violet, rhododendron, the purple aster, and *Primula farinosa*; (3) the juice of elderberries.

W. C. W.

Chromium Sesquioxide. By T. WILM (*Bull. Soc. Chim.* [2], **34**, 86).—By reducing potassium dichromate or chrome alum with alcohol and hydrochloric acid, and then precipitating the sesquioxide by ammonia, a weight of the oxide is obtained greater than that required by theory. This is attributed to a partial oxidation and formation of chromic acid.

V. H. V.

The Official Test of Quinine and Water of Crystallisation of Quinine Sulphate. By O. HESSE (*Ber.*, **13**, 1517—1520).—The method of testing quinine for cinchonidine adopted in Germany is that described in this Journal, **34**, 434. The author points out that when cinchonidine sulphate is not added as an adulterant, but is mixed by crystallisation, it then takes a form which allows some to escape detection by the above method. The author has discovered an optical method of testing quinine, by which small amounts of cinchonidine may be detected. As cinchonidine sulphate crystallises with 6 mols. H_2O , or 13.7 per cent., and pure quinine sulphate with 8 mols. H_2O , or 16.17 per cent., so the presence of cinchonidine may be detected by its influence on the percentage of water of crystallisation of a specimen. The purer the quinine sulphate, if perfectly dry and unweathered, the nearer is the percentage of water of crystallisation to 16.17. Korner states that he has obtained pure, unweathered crystals of quinine sulphate, with only 14.4 per cent. of water. The author's experience is contradictory to this statement, and he would regard such a low percentage of water as presumptive evidence of the presence of cinchonidine sulphate.

P. P. B.

Testing Commercial Sulphate of Quinine for Foreign Alkaloids. By G. KERNER (*Arch. Pharm.* [3], **16**, 186—205).—The author described in 1862 the "ammonia-method" for testing the purity of commercial sulphate of quinine: the method has been adopted very widely. A fuller account of his process is here given, together with criticisms on a method proposed by Hesse.

Hesse's process resembles the author's in not detecting less than 1 per cent. of cinchonidine sulphate, but from published results it appears to yield only an approximate estimation, whereas the ammonia-method as now described yields numbers of almost absolute accuracy. After stating his reasons for considering Hesse's process unsatisfactory, the author describes the ammonia-method with recent improvements.

The "ammonia-method" depends on the facts that a cold satu-

rated solution of quinine sulphate contains an invariable quantity of the alkaloid, and that the quantity of ammonia required to precipitate this as hydrate is constant, and that the excess of ammonia required to re-dissolve this precipitate is also constant. If the quantity of ammonia necessary to form the precipitate, and then re-dissolve it in a known volume of pure quinine sulphate solution at normal or known temperatures has been determined, the excess of ammonia required for the same quantity of a saturated solution of commercial quinine sulphate gives the means of calculating the quantity of associated alkaloids, of which cinchonidine alone is usually present. Since quinine solution readily alters by becoming mouldy, and ammonia solution also alters in strength by keeping, it is best to prepare a solution of pure quinine sulphate for each estimation, and titrate with it the ammonia to be used.

Pure Quinine Sulphate.—It is often necessary to recrystallise from three to six times, with addition of several drops of sulphuric acid in excess, in order to get rid of the last traces of cinchonidine. The purity can be tested by treating portions with different proportions of cold water and titrating the solutions with ammonia: solutions of commercial samples require different amounts of ammonia when the proportion of solvent to solid has been varied; but when pure, variations of solid to solvent between 1 : 10 and 1 : 700 produce no alteration in the quantity of ammonia required, and the excess of solid remaining undissolved in making the solutions yields also solutions of precisely the same ammonia titre.

Preparation of Solutions and Process of Titration.—The pure quinine sulphate prepared as above is rubbed into a homogeneous paste with water in a mortar and rinsed into a stoppered vessel, in which it is frequently agitated during from twelve to eighteen hours: the proportion of quinine to water used being about 1 : 100. To prepare the solution of the sample to be tested, 5 grams are similarly treated with 50 c.c. of water. The vessels containing the quinine solutions and the vessel containing the ammonia solution (of 0.92 sp. gr.) are placed in cold water, and as soon as their contents have reached the same temperature, the quinine solutions are filtered through dry filter-papers. The temperature need not be normal, provided both quinine solutions are prepared at the same temperature. The undissolved pure quinine is dried and kept for future use.

10 c.c. of each of the quinine solutions are then measured off into test-tubes, and each is titrated with the ammonia solution. 5 c.c. of ammonia solution are run in, and the test-tube is closed with the finger, and its contents are mixed by several times inverting without shaking it. The quinine is thus precipitated and almost entirely redissolved, the liquid remaining but slightly turbid; by gradually dropping in ammonia, mixing, and waiting several seconds after each addition, the moment when the liquid becomes perfectly clear is easily noted. The excess of ammonia required gives the quantity of cinchonidine sulphate present; on an average 0.288 c.c., or roughly 0.3 c.c. of ammonia solution of 0.92 sp. gr. were found to correspond to 1 mgrm. of crystallised cinchonidine sulphate. The error in the process cannot exceed 0.05 per cent.

It must be understood that this process is only directly applicable to samples which answer to the qualitative ammonia test, and which contain not more than 1·5 per cent. of cinchonidine sulphate; if more than 2 per cent. is present, the final reaction cannot be obtained, since either insoluble flocks appear or the solution gelatinises when near the clarifying point: if from a preliminary qualitative test the nature or intensity of the turbidity renders it probable that 2 per cent. or more is present, the solution to be titrated may be prepared as directed above, and then be diluted with known quantities of the pure quinine solution, or larger proportions of water to quinine may be employed in making the solution: in the latter case, it is better to warm during the process of solution.

It is noted that chemically pure quinine hydrate crystallises out from the titrated solution on standing.

An approximate estimation of the cinchonidine sulphate can be made by introducing 5 c.c. of the water extract (1 : 10, prepared at 15° C.) into a 10 c.c. cylinder graduated to tenths of a c.c., and adding 3 c.c. of ammonia of 0·92 sp. gr. On mixing by inversion, the liquid will usually remain very turbid; ammonia is then gradually added with constant mixing until the liquid becomes perfectly clear, and the total volume of ammonia added is read off. Assuming that 5 c.c. of ammonia indicate 1 per cent. of cinchonidine sulphate, and 3 c.c. indicate none, the percentage can be ascertained. This method gives with great accuracy relative values for quinine samples examined under similar conditions. This method is sufficiently accurate for practical purposes, the former more exact method being resorted to for disputed cases and for scientific purposes only.

Quinidine is seldom present, except as an adulterant purposely added; it dissolves somewhat more readily in excess of ammonia than cinchonidine does.

The percentage of water, present as water of crystallisation or otherwise, is of considerable importance, both for commercial reasons and to ensure the correctness of quantities of the alkaloïd used as doses. The presence of a small quantity of sulphuric acid tends to promote crumbling of the crystals with loss of their water of crystallisation, whilst a small amount of uncombined water tends to prevent this change. Uncombined water is estimated by the difference between the quantities of water found on drying a portion of the original sample and another portion which has been pressed between soft blotting-paper. The author, after a long experience in estimating water in quinine, considers that in the crystalline condition its formula is $2C_{20}H_{24}N_2O_2 \cdot H_2SO_4 + 7H_2O$: when dried at 115° C. it loses 14·45 per cent. of water: in practice the loss varies between 14·38 and 14·8. A good sample will usually not lose more than 13·8 to 14·4 per cent. by drying, but no sample should lose more than 14·6 per cent. without exciting suspicion.

If left for some time in a dry and moderately warm situation, the crystallised sulphate loses nearly $5H_2O$ ($= 10·32$ per cent.), leaving $2C_{20}H_{24}N_2O_2 \cdot H_2SO_4 + 2H_2O$, which contains 4·60 per cent. of water. In this form, the salt is less presentable in appearance, but is permanent at temperatures below 100° C.: the sulphate would be well

suited for pharmaceutical purposes in this condition, since it is not liable to loss or absorption of moisture, and contains a maximum amount of 5 per cent. of water: it would also be impossible to moisten it without altering its appearance. Another means of avoiding the inconvenience arising from the variation in composition which is noticed in the ordinary commercial sulphate, would be to replace it by the hydrochloride, which is a far less variable salt, and is also more easily assimilated. As long as the crystallised sulphate is used, it is necessary to estimate the percentage of water in every sample in determining its value.

The percentage of water is estimated either by finding the quantity of anhydrous alkaloid, and then calculating from the formula the quantity of water as recommended by Dwars (*Arch. Pharm.*, **11**, 149), or better, by directly estimating the loss of water, when from 1 to 2 grams are dried by heating very gradually to 115° C. F. C.

Butter Analysis. By L. MEDICUS and others (*Bied. Centr.*, 1880, 615—617).—The authors have examined Reichert's method of estimating adulteration in butter, and confirm the results already obtained by him. Donny recommends as an easy method of detecting adulteration to heat a sample of butter in a test-tube at 160°; if the butter is pure it foams very much, and becomes of a uniform brown colour; if impurities are present there is very little swelling, but the liquid bumps violently, and casein separates out on the sides of the tube in brown masses, whilst the rest of the butter retains its original colour.

J. K. C.

Technical Chemistry.

The Changes Undergone by Meat in the Process of Pickling. By Vorr (*Zeits. Biologie*, **15**, 492—495).—Rubner (*Zeits. Biologie*, 1877, **13**, 513) found that meat, when pickled, lost no albuminoids and only 11 per cent. of its phosphoric acid.

The author treated 926 grams of meat with a brine containing 60 grams of common salt for 14 days.

The meat originally contained 702·8 grams of water, and 223·2 grams of solid residue; the residue yielded 211·1 grams of organic matter and 12·04 grams of ash, with 4·12 grams of phosphoric acid. After 14 days, the brine contained 22·48 grams of dry residue with the composition:—

	Total.	Per cent.	Meat lost per cent.
Organic matters.....	4.47	19.88	2.1
Albumin.....	2.18	9.68	1.1
Extractives	2.29	10.19	13.5
Ash.....	18.01	80.12	—
NaCl	16.08	71.50	—
Phosphoric acid.....	0.35	1.56	8.5

The meat when taken out weighed 892.3 grams, indicating a loss of 33.7 grams; the dry residue of the meat weighed 270.5 grams, *i.e.*, the salt meat contained 30.31 per cent. solid and 69.69 per cent. of water.

1,000 parts of fresh meat would from these results be affected by salting as follows:—

It would take up 43 grams salt.

It would lose 19.7 grams water = 10.4 per cent.

„ 4.8 „ organic matter = 2.1 „

„ 2.4 „ albumin = 1.1 „

„ 2.5 „ extractives = 13.5 „

„ 0.4 „ phosphoric acid = 8.5 „

The author is of opinion that meat is by no means so seriously deteriorated as a food by salting as is generally supposed.

W. N.

Analyses of Gluten Bread. By K. BIRNBAUM (*Bied. Centr.*, 1880, 370—311).—The preparation of bread from the gluten of wheat for the use of persons suffering from diabetes is of considerable importance. Boussingault examined some samples and declared them unsuitable, but the author's investigations show that he must have examined inferior qualities, and that his condemnation should not extend to all kinds. The German preparations show a large proportion of protein substance and a small one of carbohydrates.

J. F.

Hair-dyes. By J. F. BRAGA (*Chem. News*, 42, 8).—A solution of silver nitrate (10 grams per litre) when used for some time as a hair-dye produces a dull reddish-brown tint. This is particularly noticeable when the light falls very obliquely. This defect is avoided by adding a small quantity of copper solution to the silver nitrate; 36 grams of silver nitrate and 2.5 grams of copper sulphate are dissolved in 250 c.c. of water, sufficient ammonia to redissolve the precipitate, and the whole made up to 1 litre with water.

An “instantaneous dye” is obtained by treating the hair first with a solution of pyrogalllic acid, made strongly acid with acetic acid, and when it is almost dry, the silver and copper solution of the above strength is added. All shades from brown to black may be obtained by varying the strength of the pyrogalllic acid from 1 to 50 grams per litre.

L. T. O'S.

Composition of Ink. By W. THOMPSON (*Chem. News*, 42, 32—33).—The author finds that in the testing of inks, the following re-

agents are the best:—Dilute sulphuric acid, strong hydrochloric acid, dilute nitric acid, sulphurous acid, caustic soda, oxalic acid, bleaching powder, stannous and stannic chlorides.

Ink, prepared by the same maker at different times, gives different results. Black inks, when treated with dilute sulphuric acid, behave very differently, some giving shades from a bright crimson to a deep red, whilst others give a blue-green, violet, or grey.

The reactions given by the same ink with the same reagent vary according to the length of time which has elapsed since the ink was used. The length of time that an ink is exposed to sunlight also influences the character of the reaction, as does the use of steel pens.

L. T. O'S.

Combustibility of Tobacco. By E. QUAJAT (*Bied. Centr.*, 1880, 345—347).—The author examined 14 specimens of tobacco, consisting of common and fine sorts. The percentage of ash to dry substance varied from 31·05 in a Bassano sample down to 17·11 in Virginian and 16·78 in a sample of Turkish. The author rules that the finer the quality the smaller is the amount of ash. (Nessler, however, says that there is no relation between the two.)

The composition of the ash is of the most variable character, and in the most easily combustible, potassium salts seem to predominate over other mineral salts. Some samples, which burned with difficulty, were improved by steeping in a solution of potassium salts and organic acids, but others were not so improved. The author recommends the study of this point to tobacco manufacturers. He agrees with Nessler that the amount of nicotine present has no effect on the combustibility.

Composition of the Ash of 5 Samples of Tobacco.

	Virginia cigars.	Sella cigars.	Beneventon leaves.	Virginia leaves.	Bot. Gar., Padua.
Silicic acid	2·55	2·99	0·00	0·00	0·95
Lime	26·64	28·70	27·99	—	37·49
Magnesia	47·69	6·93	1·74	—	4·96
Phosphoric acid	2·97	3·61	5·28	—	6·91
Sulphuric anhydride	4·21	3·80	4·23	7·56	3·63
Carbonic "	20·82	19·98	20·09	19·26	25·26
Ferric oxide	3·27	2·79	4·71	—	1·27
Chlorine	6·55	3·78	7·14	8·47	1·06
Potash	20·01	21·27	24·15	—	11·75
Soda	5·77	7·03	3·89	—	5·33

J. F.

General and Physical Chemistry.

Relative Intensity of the Spectral Lines of Hydrogen and Nitrogen; its Bearing on the Constitution of Nebulæ. By C. FIEVEZ (*Ann. Chim. Phys.* [5], 20, 179—185).—Observations by Huggins have shown that in the spectra of certain nebulæ there exists only one nitrogen line and one hydrogen line, and further researches by the same physicist have proved that the complex spectrum of nitrogen can be readily simplified by merely diminishing its intensity, so that it is possible to extinguish a portion of the luminous rays, and to leave visible only those which are observable in the nebular spectrum.

Adopting a method similar to that originally devised by Huggins, the author has also succeeded in showing that if the hydrogen spectrum be reduced in intensity, the line F, which corresponds with that of the nebulæ, will alone remain visible after the C and other more refrangible lines have become too weak to affect the eye. The method employed consisted in projecting by means of a lens a real image of the luminous body on the slit of the spectroscope, and afterwards altering the intensity of this image, either by diminishing the aperture of the lens used for projection, or by placing a diaphragm with a circular opening between the lens and the image.

The hydrogen tube was one of Plücker's, entirely covered with lamp-black, with the exception of a small portion of the contracted part, and was placed vertically before the projection lens. The distances from the tube to the lens and from the latter to the slit were arranged in such a manner that the projected image was narrower than the length of the slit, so that the luminous pencil, after it had passed through the slit, was received in its entirety upon the objective of the spectroscope. This arrangement, which is due to Lockyer, enables the observer to distinguish between long and short lines. With a powerful induction coil and condenser arranged for tension, and with a six-prism spectroscope, the hydrogen lines C, F, and H, are perfectly visible; the luminous pencil was then narrowed gradually by means of a diaphragm of 0·007 meter aperture, by withdrawing the diaphragm from the slit and bringing it nearer to the lens. The length of the lines was seen to diminish, and the H line finally became invisible, whilst the other two lines still remained brilliant. With a diaphragm of 0·002 meter aperture the C line also disappeared, leaving the F line alone visible. With a small induction coil without a condenser, and a two-prism spectroscope, the same results may be obtained, but less rapidly than with more powerful instruments.

The line spectrum of nitrogen, called also a spectrum of the second order, is formed of several groups of lines indicated by Plücker by the numerals 1, 2, 3, 4, and 5. With the large coil and spectroscope, and a 0·007 meter diaphragm as before, the groups 1, 3, 5, 2, successively

disappear, and group 4 is extinguished, with the exception of the double line coinciding with that of the nebulae. If, while the experiment is proceeding, and when a line or group of lines have just been rendered invisible, the width of the slit of the spectroscope be slightly increased, the extinguished line immediately reappears, thus showing plainly that the disappearance is due, as was anticipated, to the weakening of the luminous intensity of the ray. We are therefore at liberty to consider with Huggins that certain nebulae do contain nitrogen and hydrogen among their constituent elements, referring the relative invisibility of the other rays to the absorptive action of space.

J. W.

Fluorescence. By O. LUBARSCH (*Ann. Phys. Chem.* [2], **11**, 46—69).—The paper describes the author's researches on fluorescence, in which he has repeated the experiments of Hagenbach with certain modifications in the spectroscopic apparatus, whereby light of greater homogeneity is obtained. From the numerous experiments and observations adduced in the paper, the author's conclusion is that Stokes's law can no longer be maintained as a universally valid principle.

R. R.

Thermic Theory of Electricity. By J. L. HOORWEG (*Ann. Phys. Chem.* [2], **11**, 133—155).—In this paper, the author continues to adduce experiments and reasonings in support of the view which regards the molecular motion of heat as the source of electrical energy. He conceives that when any disturbance of the motions of the molecules occasions a loss of their *vis viva* an equivalent quantity of electricity appears. Among the propositions discussed are the following:—The division of bodies into classes, according as their conductivity is distinguished as metallic or electrolytic, is artificial. A current arises when at least one of the substances in a closed circuit has its conductivity increased by rise of temperature. The electricity of friction and pressure arises from the contact of heterogeneous substances, by which the loss of molecular *vis viva* is occasioned. Friction simply increases the intimacy of the contact by multiplying the points at which the bodies touch, and it unequally raises the temperature of both substances, thus producing conditions which co-operate in augmenting the effect. The electricity of friction and pressure has the same origin as that of the pile, viz., a disturbance of the molecules occasioning a loss of their *vis viva*. The theory is applied to pyro-electricity, thermo-electricity, and the electrical phenomena observed in evaporation, solidification, solution, cleavage, division, osmose, and capillary action.

R. R.

Discharge of Electricity in Gases and High Vacua. By F. NARR (*Ann. Phys. Chem.*, **11**, 155—163).—The paper describes experiments in continuation of a former research on the passage of electricity through the vacua obtained by the Sprengel mercury pump. Glass tubes were not employed on account of their uncertain and changeable electrical properties, the vessel used being a hollow brass sphere. The results appear to show that electricity traverses

the gas-vacuum, but the author remits their full discussion to a forthcoming communication.
R. R.

Electrical Conductivity of Saline Solutions. By J. H. LONG (*Ann. Phys. Chem.* [2], 11, 37—46).—The author has continued the investigations of Kohlrausch on the conductivity of saline solutions at different temperatures and states of concentration. The salts examined were the chlorides of manganese and zinc, and the nitrates of copper, strontium, and lead. The results, of which tables and graphic representations are given, are discussed in relation to the observations of other experimenters.
R. R.

Vapour-tensions of Homologous Series and Kopp's Law of Constant Difference of Boiling Points. By A. WINKELMAN (*Annalen*, 204, 251—264).

The Law of Corresponding Boiling Points. By U. DÜHRING (*Ann. Phys. Chem.* [2], 11, 163—170).—The correctness of a law brought forward by the author having been questioned by A. Winkelman (*ibid.* [2], 9, 391), the present paper is devoted to its defence. The law in dispute may be represented by the equation—

$$\frac{t'_p - t_p}{t'_p - t_p} = \frac{q'}{q}$$

where t_p and t'_p are the boiling points of a liquid under the pressures p and p' respectively, and t_p and t'_p those of another liquid under the same pressures, while q and q' are constants depending upon the two liquids.
R. R.

Volume Relations of some Haloïd Salts. By W. MÜLLER ERZBACH (*Ber.*, 13, 1658—1660).—The author has previously pointed out that the contraction taking place when chlorine, bromine, and iodine combine with metals is most considerable in the case of chlorine, and least with iodine. He now confirms his previous observations by calculating the contraction from a number of new data obtained by various observers. These are given in the following table:—

Name of salt.	A. Sp. gr.	Observer.	B. Mol. weight.	C. Calc. volume.	D = $\frac{B}{A}$. Volume found.	E = $\frac{C}{D}$. Condensa- tion.	F = $\frac{C-D}{C}$. Contraction.
RbCl ...	2·20	Clarke	120·9	81·7	55·0	1·49	0·32
RbBr ...	2·78	do.	165·4	81·7	59·8	1·36	0·27
RbI ...	3·02	do.	212·4	81·7	70·0	1·17	0·14
LiCl ...	1·998	Kremer	42·5	37·4	21·2	1·76	0·43
LiBr ...	3·10	Clarke	87·0	37·4	28·1	1·34	0·25
LiI ...	3·49	do.	134·0	37·4	38·5	0·97	—0·03
CdCl ₂ ...	3·94	Knight	183·0	64·2	46·5	1·38	0·27
CdI ₂ ...	5·98	Fullerton	366·0	64·2	61·0	1·05	0·05

Inorganic Chemistry.

A Source of Atmospheric Carbonic Anhydride. By M. S. MEUNIER (*Bied. Centr.*, 1880, 633—634).—According to Cloez, iron which contains carbon and manganese yields carbonic anhydride on treatment with hot water; this reaction may be assumed to go on in the neighbourhood of hot springs in metalliferous districts, and thus to be a source of atmospheric carbonic anhydride. J. K. C.

Liquid Sulphur Phosphide. By H. SCHULZE (*J. pr. Chem.* [2], **22**, 113—130).—After referring to the experiments of Berzelius and Ramme (*Ber.*, **12**, 1350), the latter of whom observed that there was no rise of temperature when phosphorus and sulphur were combined under warm water, and that on distilling the liquid product with steam, phosphorus passes over, leaving sulphur with a smaller proportion of phosphorus behind. The author says he has repeated the experiments and can confirm these observations, for not only was there no rise, but there was a slight fall of temperature on bringing sulphur and phosphorus together under water at 20°. On cooling the liquid of the composition P_4S , it was found to deposit crystals of phosphorus which redissolved when the temperature rose to 15°, but separated out on again cooling. Liquid P_2S deposited sulphur crystals. Wicke (*Ann. Chem. Pharm.*, **86**, 115) had found that sulphur dissolved in P_4S is deposited again on long standing in a cool place.

Contrary to what is stated by Berzelius, the author finds that phosphorus volatilises, when heated at 100° in a stream of hydrogen, whilst the hydrogen is partly converted into phosphine. The author did not succeed in effecting complete separation in this manner, as sometimes below and sometimes above 100°, a reaction took place in the liquid, causing an explosion. After a less violent reaction he has, however, occasionally succeeded, by very gradually heating small quantities in the paraffin-bath, in removing phosphorus, far below its boiling point, in a current of carbonic anhydride, and obtaining a residue of solid sulphur phosphide.

The author finds, contrary to Gmelin-Kraut's notice, that carbon bisulphide is incapable of dissolving out the phosphorus from the sulphur; but he succeeded in effecting a partial separation by dissolving in carbon bisulphide, and then agitating the concentrated solution with alcohol, ether, chloroform, light petroleum, or other liquids, miscible with carbon bisulphide, but of slight solvent power for sulphur, when most of the sulphur is separated, and a liquid produced containing more or less sulphur in solution, according to the amount of carbon bisulphide present. Phosphorus is also precipitated from its solution in carbon bisulphide by these reagents, so that it is only at first that pure sulphur is deposited.

R. Böttger (*J. pr. Chem.*, **12**, 358) found that by shaking transparent phosphorus with potassium polysulphide, and allowing it to stand for four days in a dark place, transparent sulphur phosphide was

produced. This the author can confirm, as also the decomposition of hydrogen persulphide by transparent phosphorus.

In reviewing the facts as thus presented, it would seem that these sulphur phosphides are not chemical compounds, as there is no evolution of heat on their formation, moreover they are readily decomposed by lowering the temperature, by solvents, and by heating in a current of gas. The decomposition of the potassium polysulphides and of hydrogen persulphide by phosphorus seems to point the other way, but similar actions are seen in crystalline salts giving up their water of crystallisation to the air, and the fact observed by Schöne (Gmelin-Kraut, 2, 38), that alcohol precipitates potassium tetrasulphide from a concentrated solution of the pentasulphide, dissolving sulphur (and polysulphide).

Since neither phosphorus nor sulphur by itself can decompose water, it seems remarkable that a simple mixture of the two should have the power. But there are several examples which show that two bodies acting in common on a third, need by no means be combined. The action of chlorine and carbon on alumina is a case in point. The liquefaction of solid salts soluble in water, by contact with ice, is perfectly analogous to the formation of the liquid sulphur phosphide from its elements.

F. L. T.

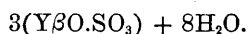
The Earths of Samarskite. By C. MARIGNAC (*Ann. Chim. Phys.* [5], 20, 535—557).—In this memoir, the author describes only those oxides which form nitrates of relative high stability, and have been separated from those oxides, such as erbia, ytterbia, &c., which form nitrates easily decomposed by heat. They have been separated one from another by taking advantage of the different solubilities of their double sulphates with potassium in a saturated solution of potassium sulphate. Details of this and other methods of separation employed, are given. The earths present in samarskite (from North America) were thus divided into four groups:—

I. *Double Sulphates Soluble in less than 100 vols. of K_2SO_4 Solution. Molecular weight rises to 119.*—Yttria and terbia, with traces of the oxides of decipium and didymium, and probably traces of the oxide of $Y\alpha$ found in Group II. The terbia, even after strong ignition, had a faint chamois tint, which disappeared on heating in a current of hydrogen, and reappeared when the oxide was again heated in the presence of air. These changes of colour were accompanied by very slight variations in weight.

II. *Double Sulphates soluble in 100—200 vols. of K_2SO_4 Solution. Molecular weight varies between 119 and 120.*—This portion consisted mainly of the oxide of a metal which the author provisionally designates $Y\alpha$. Its molecular weight is about 120.5, a maximum between the molecular weights of those earths which most nearly approach it in their behaviour with potassium-sulphate solution. It forms colourless salts, the solutions of which show no absorption spectrum. It is distinguished from all the metals of this class except yttrium and ytterbium by the very faint orange-yellow colour of its oxide, and by the fact that its salts show no absorption spectrum: from yttrium by the sparing solubility of its formate, and of its double potassium

sulphate; from ytterbium by the much greater stability of its nitrate, and the ease with which the ignited oxide dissolves in dilute acids. Yz is probably identical with that base, the existence of which has been indicated by Delafontaine (*Compt. rend.*, 90).

III. *Double Sulphates very slightly soluble in K_2SO_4 Solution.* *Molecular weight falls from 119 to 115 as the Solubility decreases.*—This group contains the oxide of $Y\alpha$, a small quantity of the oxide of didymium which cannot be completely separated, and the oxide of a metal of $Y\beta$, which forms a nitrate readily decomposed by heat, but is included in this group, because its double potassium sulphate is very sparingly soluble in K_2SO_4 solution. The molecular weight of the oxide of $Y\beta$ is probably somewhat lower than 115.6. Its sulphate forms small, short, crystals similar to those of the sulphates of yttrium and didymium, but of a sulphur-yellow colour; they have the constitution—



Solutions of the salts of this base give a well-defined absorption spectrum which closely resembles that ascribed by Delafontaine to decipium, or, still more closely, that described by Boisbaudran as peculiar to the new element samarium. Since these three bodies were obtained from samarskite by the same methods, it is probable that they are essentially one and the same substance. The molecular weight of the oxide of decipium is, however, according to Delafontaine, 130, whilst that of the oxide of $Y\beta$ is below 115.6. Further, the salts of decipium are colourless, those of $Y\beta$ have a yellow colour, the intensity of which increases the further the purification is carried. Probably either the substance obtained by Delafontaine is mixed with a considerable proportion of some other base having a high molecular weight, or that obtained by the author contains a base forming yellow salts, and having a much lower molecular weight. Further investigations are necessary to decide this point.

IV. *Double Sulphates insoluble in K_2SO_4 Solution.*—This group contained only didymium, which, however, could not be completely purified from traces of other metals.

Some of the products, particularly those most soluble in K_2SO_4 solution, contained traces of a substance which formed a yellowish oxide and is probably identical with the philippium of Delafontaine.

The author has attempted to determine the relative solubilities of the formates of the metals present in samarskite and similar minerals, but without success. The solubility of these salts varies very greatly with the mechanical treatment to which they are subjected, and their solutions readily assume a state of supersaturation which they retain for a considerable length of time, even when in contact with the solid salt.

C. H. B.

Metallic Oxides of the Iron Group. By H. MOISSAN (*Ann. Chim. Phys.* [5], 21, 199—255).—*Iron.*—The black pyrophoric powder obtained by heating ferrous oxalate, or ferric oxide in a current of hydrogen or carbonic oxide, consists of ferrous oxide, and contains no metallic iron, or only traces.

The reduction of ferric oxide in a current of hydrogen commences a little above 330° ; between this temperature and the boiling point of sulphur, 440° , the product is triferrous tetroxide, Fe_3O_4 . The same oxide is obtained when hydrated or anhydrous ferric oxide is heated to the melting point of zinc, 420° , in a current of pure and dry carbonic oxide. If the carbonic oxide contains carbonic anhydride, a small quantity of ferruginous carbon is deposited. Between 500° and 600° ferrous oxide FeO , pyrophoric at ordinary temperatures, is obtained. The results are the same even if the ferric oxide be mixed with a considerable proportion of alumina. By heating ferrous oxide to the softening point of glass in a current of hydrogen, metallic iron is obtained, but it is more or less agglutinated and is not pyrophoric. It is evident that the reduction of ferric oxide to metallic iron takes place in well-defined stages. When ferric oxide is heated to dull redness in a current of carbonic oxide, a more or less agglutinated powder is obtained, which is not pyrophoric, and dissolves in dilute sulphuric acid with evolution of hydrogen, leaving a residue of carbon. Pyrophoric metallic iron may, however, be obtained by heating ferric oxide in a current of perfectly dry hydrogen at 440° for a very long time, *i.e.*, several days; or by distilling iron amalgam at the lowest possible temperature. In all these cases of reduction, it is necessary, in order to obtain good results, that the reducing gas should be as pure and as dry as possible, and the current should be somewhat rapid.

In addition to the methods above described, ferrous oxide may be prepared by heating ferrous oxalate out of contact with the air. That the pyrophoric black powders obtained in these experiments and shown by analysis to correspond in composition with FeO were really ferrous oxide, and not mixtures of triferrous tetroxide with metallic iron was proved by the fact that they gave no hydrogen when treated with dilute acids, and did not decolorise an aqueous solution of iodine. When ferrous carbonate is heated out of contact with air, triferrous tetroxide, Fe_3O_4 , is formed. Now, when carbonic anhydride is passed over heated ferrous oxide, carbonic oxide and triferrous tetroxide are produced. It is probable therefore that the ferrous carbonate first splits up into ferrous oxide and carbonic anhydride, which react on each other in accordance with the equation $3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$. If the ferrous carbonate be heated slowly in a current of nitrogen, ferric oxide is formed: if rapidly heated, a small quantity of pyrophoric ferrous oxide is produced.

Allotropic Modification of Triferrous Tetroxide.—In addition to the methods described above, triferrous tetroxide may be obtained by heating ferric oxide, or metallic iron reduced by hydrogen, to redness in a current of hydrogen saturated with aqueous vapour at 90° ; by heating ferrous carbonate to dull redness in a current of carbonic anhydride; and by heating reduced iron in a current of carbonic anhydride at 440° . As thus prepared at low temperatures, it is a black magnetic powder, density 4.86, is readily attacked by concentrated nitric acid, and when heated becomes incandescent, forming Fe_2O_3 . This is one modification of triferrous tetroxide. When the ferric oxide produced by heating this modification is exposed to a high temperature, about 1500° , it gives off oxygen, and is reconverted into

triferrous tetroxide, a black magnetic substance, sp. gr. 5 to 5.09, almost unattacked by boiling concentrated nitric acid, and not forming ferric oxide when heated; it is, in fact, the most stable oxide of iron. When the first modification of the triferrous tetroxide is heated to whiteness in a current of nitrogen, it agglomerates, increases in density, no longer forms Fe_2O_3 when heated, and has all the properties of the second modification. It is evident that there are two well-defined allotropic forms of triferrous tetroxide, one formed at low, the other at high temperatures. The author explains the fact that the modification β formed at high temperatures does not give ferric oxide when heated, by assuming that when the modification α , formed at low temperatures, is converted into ferric oxide, the heat evolved is less than that evolved when the modification α is converted into the modification β , and therefore the formation of ferric oxide from the latter would be an endothermic reaction.

Allotropic Modifications of Ferrous Oxide.—When prepared at temperatures below 600° , ferrous oxide is a pulverulent, ivory-black substance, which readily burns in the air, forming Fe_2O_3 , the temperature of the combustion being sufficiently high to convert a portion of the Fe_2O_3 into Fe_3O_4 . It is oxidised with incandescence by nitric acid, burns, when gently heated in nitrogen monoxide or dioxide, displaces ammonia from its combinations, and decomposes water slowly at ordinary temperatures, more rapidly at 100° . If, however, it be obtained at a high temperature, as for example, by heating reduced iron in a current of carbonic anhydride, it is not pyrophoric at ordinary temperatures, and is converted into triferrous tetroxide when burnt. When pyrophoric ferrous oxide is heated in an atmosphere of nitrogen to the melting point of silver, it loses its pyrophoric properties, is not attacked by dilute acetic acid, and when heated burns like tinder, forming Fe_3O_4 . Further, when the modification of ferrous oxide formed at low temperatures is heated in a current of carbonic anhydride, it is converted into the low temperature modification of triferrous tetroxide, but the high temperature modification of ferrous oxide, when heated, gives the β or high temperature modification of triferrous tetroxide.

Manganese.—When manganese dioxide, obtained by calcining manganous nitrate, is heated at 280° in a current of hydrogen, it becomes incandescent, and is reduced to the monoxide MnO . The reduction of the dioxide commences at 230° , and if the temperature is kept constant at this point, manganese sesquioxide, Mn_2O_3 , having a deep maroon colour, is obtained. At a somewhat higher temperature trimanganic tetroxide, Mn_3O_4 , is formed, and this, when carefully heated in the presence of air, is converted into the sesquioxide which, when strongly heated, gives trimanganic tetroxide, unalterable by heating in contact with air. When the trimanganic tetroxide obtained at a low temperature is heated at 260° in a current of pure and dry hydrogen, it is rapidly reduced with formation of the monoxide, a green powder which oxidises rapidly, and if previously heated to 140° takes fire when thrown into the air. Out of contact with air, this oxide is but slightly acted on by water, but in presence of air it quickly oxidises. A non-pyrophoric variety of the monoxide has been obtained by Deville in

regular octohedra of a beautiful green tint, by reducing a higher oxide at a red heat in a current of hydrogen containing hydrochloric acid.

When the crystalline amalgam of manganese obtained by electrolysis, is distilled at 440° in a current of pure hydrogen, a light, porous, blackish grey mass of metallic manganese is left. It is oxidised with incandescence by nitric acid, and portions of it take fire when thrown into the air.

Nickel.—Hydrated or anhydrous nickel sesquioxide, Ni_2O_3 , heated at 190° in a current of hydrogen, is reduced to the grey magnetic oxide, Ni_3O_4 . At a somewhat higher temperature the yellowish-green monoxide is obtained. This undergoes no further change at 200° , but at 230 — 240° is reduced to metallic nickel, in the form of a black powder, which is pyrophoric at ordinary temperatures, but does not burn so brilliantly as metallic iron reduced at 440° . That the temperature of combustion is not very high is shown by the fact that the product consists mainly of the sesquioxide, whereas the only oxide stable at a high temperature is the monoxide.

When nickel amalgam is distilled in a current of hydrogen at the lowest possible temperature, the nickel obtained is not pyrophoric.

Nickel monoxide obtained by reduction is green when cold, yellow when hot. It readily absorbs oxygen even at ordinary temperatures, and is partially converted by nitric acid, with elevation of temperature, into the sesquioxide, which dissolves in acids with evolution of oxygen. The monoxide when heated in air or oxygen to 350 — 440° , forms a blackish powder, the composition of which depends on the temperature; at 600° this black powder is reconverted into the monoxide, showing that the higher oxides of nickel can only exist below a certain temperature. Nickel monoxide dissolves in hydrochloric and sulphuric acids, with rise of temperature; it forms a beautiful violet solution with ammonia, and displaces ammonia from its salts.

Cobalt.—The sesquioxide is reduced at the same temperature as nickel sesquioxide, viz., 190 — 200° . At 250° metallic cobalt is obtained in the form of a black powder, which takes fire at ordinary temperatures, forming mainly the oxide Co_3O_4 . If the reduction takes place at 700° , the metallic cobalt is never pyrophoric; and the metal obtained by distilling the amalgam in hydrogen at the lowest possible temperature behaves in the same way.

Cobalt monoxide obtained by reduction is a dark coloured, readily oxidisable powder, which when slightly heated in presence of air, becomes incandescent, and is converted into the sesquioxide. The sesquioxide at a higher temperature forms the magnetic oxide, Co_3O_4 , and this when still further heated gives the monoxide, CoO , the oxide stable at high temperatures.

Chromium.—The sesquioxide is not reduced by hydrogen at any known temperature. When strongly heated, it becomes incandescent, and is rendered almost insoluble in acids. The ignited oxide when heated at 440° in a current of hydrogen sulphide, dry chlorine, oxygen, or bromine vapour, undergoes no change whatever.

When the non-ignited oxide is heated at 440° in a current of hydrogen sulphide, it forms chromium sesquisulphide, the properties of which have been previously described by the author (this Journal,

Abstr., 1880, 527). Heated in a current of oxygen, the sesquioxide is oxidised to the dioxide, CrO_2 , as already pointed out by Krüger. This dioxide has a deep grey colour, and when calcined evolves oxygen and is reconverted into the sesquioxide. When heated with hydrochloric acid or a mixture of sulphuric acid and sodium chloride, chlorine is given off. Fused with potash, out of contact with air, it gives potassium chromate and chromium sesquioxide.

When the hydrated sesquioxide is gradually heated in a current of chlorine, it first loses water, and at 440° is converted into chromyl dichloride. The dehydrated but not ignited sesquioxide is partially converted into chromic chloride, but no chromyl dichloride is formed; if, however, the chlorine be saturated with aqueous vapour at $8-10^\circ$, the latter compound is formed in considerable quantity. If the chlorine be saturated with aqueous vapour at 20° , but little chromyl dichloride is produced. Chromyl dichloride is also formed when a current of moist chlorine is passed over chromic chloride heated at 440° , but a moist inert gas, such as carbonic anhydride, does not produce this change. Further, it is found that the hydrated sesquioxide when dried at 440° contains 5—10 per cent. of water. Probably in all these cases chromic chloride is first formed, and then decomposed with production of chromyl dichloride, by the excess of chlorine, and the water present either in the gas or in the oxide.

By arresting the action of moist chlorine on the chromium sesquioxide at the moment when the red vapours of CrO_2Cl_2 are given off, a brown powder is obtained, which approaches in composition the oxychlorides described by Moberg.

Bromine vapour, under the same conditions, also attacks the non-ignited chromium sesquioxide.

Chromium amalgam may be obtained by the action of sodium amalgam on the chloride, bromide, or iodide of chromium. Like the amalgams of all the metals of this group, it oxidises readily. When distilled in a current of hydrogen at the lowest possible temperature, metallic chromium is left in the form of a black, amorphous, very slightly agglutinated substance, which takes fire when exposed to the air. If distilled at temperatures above 355° , the residual chromium is not pyrophoric. The chromium thus obtained is more readily oxidised, and is more soluble in acids than that obtained by Deville by reducing the sesquioxide with carbon. When heated to dull redness in a current of dry carbonic anhydride, it is converted into the sesquioxide.

If this family of elements be arranged in the order, chromium, manganese, iron, cobalt, nickel, their affinity for oxygen and the heats of formation of the oxides, chlorides, bromides, iodides, and sulphides decrease as the atomic weight increases. C. H. B.

Atomic Weight of Antimony. By R. SCHNEIDER (*J. pr. Chem.* [2], 22, 131—147).—A controversial paper in reply to strictures passed by Kessler on the author's results.

The author, together with Cooke, finds 120 as the atomic weight; Kessler, in common with Dexter and Dumas, obtains 122.

The author's method is by reduction of a pure specimen of antimony

glance by hydrogen, and in 1856 (*Pogg. Ann.*, **98**, 293—308) obtained 120·3 by this means.

The author gives three recent determinations made on the same plan, and with an antimony glance containing—

Antimony sulphide.	Insoluble residue		Calcium carbonate.	Ferrous sulphide.
	(quartz).			
99·811	0·108		0·048	0·033

As on heating it in a current of hydrogen or carbonic anhydride it decrepitated, giving out a slight empyreumatic odour, it was heated before reduction in hydrogen to 290—320° until decrepitation had ceased and the issuing gas was odourless. Antimony sulphide itself undergoes no reduction at this temperature.

The mean result from the three experiments is 120·182, which compares well with 120·3, the one previously obtained.

Dexter, like Berzelius, determined the atomic weight by oxidation of the metal with nitric acid and ignition of the residue. The supposition that the residue on ignition is a thoroughly stable body of the composition of antimony tetroxide is incorrect, as Bunsen has shown (*Annalen*, **192**, 317).

Kessler's method (*Pogg. Ann.*, **95**, 204 (1855), and **113**, 134 (1861)) is to oxidise antimonious chloride in concentrated hydrochloric acid by a volumetric solution of potassium dichromate in excess, and to add, after dilution of the solution, an excess of ferrous chloride and then titrate back the excess of ferrous chloride by chromium solution. In 1855 he obtained the atomic weight 123·7, and in 1861 one experiment with antimony, one with antimony trioxide, and a third with antimonious chloride, gave 122·29.

The author criticises Kessler's method, and infers that no reliance is to be placed on it.

F. L. T.

Products of Decomposition and Metamorphosis of Uranyl Sulphide. By C. ZIMMERMANN (*Annalen*, 204—224).—Uranium does not exhibit a great affinity for sulphur, since uranyl sulphide is converted into uranyl hydroxide by washing with warm water. It has been noticed by Remelé (*Pogg. Ann.*, **124**, 120) that when uranyl sulphide is left in contact with ammonium sulphide the liquid becomes of a brown to deep black colour. The author shows that this is due to the solubility of the uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When precipitated uranyl sulphide is left for a long time in contact with ammonium sulphide in the cold, two bodies are obtained, one red the other black. The author shows that when the ammonium sulphide contains a considerable amount of thiosulphate the red body is formed, but that in absence of thiosulphate the black body is obtained. The thiosulphate is formed by the action of atmospheric oxygen on the ammonium sulphide. The formula assigned to uranium-black is $\text{Ur}_2\text{O}_2 < \overset{\text{O}}{\text{O}} > \text{Ur} + 2\text{Ur}_2\text{O}_3$.

Uranium-red seems to consist of an oxygen-compound which contains, besides sulphur, a second base (potassium, sodium, ammonium, or barium), and some uranium, probably as uranyl sulphide. Anhydrous

uranium-red, on the assumption that it is perfectly free from admixture,
 may be formulated thus: $U_6SK_2O_9 = 2Ur_2O_3 + Ur_2O_2 < \begin{smallmatrix} OK \\ SK \end{smallmatrix}$.

G. T. A.

Mineralogical Chemistry.

Analysis of the Mineral Water of Niederbronn in Unter-Elsass. By E. BURI (*J. pr. Chem.* [2], 22, 388—395).—The water as it runs into a large basin from the spring appears deep green, occasional bubbles of gas escape; it is perfectly clear at first, but appears turbid when removed.

The sample was collected on 5th June, 1880; its temperature then was 17·9°, that of the air being 11·6°. Its sp. gr. at 16·4° was 1·0036, taste saline and somewhat inky; no smell was noticeable. With test-paper the reaction for carbonic acid was given.

In 10,000 parts by weight of the water there were contained:—

Strontium sulphate	0·250
Calcium sulphate	0·697
Potassium chloride	2·187
Sodium chloride	30·748
Lithium chloride	0·274
Ammonium chloride	0·088
Calcium chloride	6·621
Magnesium chloride	2·456
Calcium bicarbonate	3·900
Magnesium bicarbonate	0·049
Ferrous bicarbonate	0·104
Silica	0·135
	<hr/>
	47·509
	<hr/>
Free carbonic anhydride....	0·794
Nitrogen	0·328

There were also present traces of phosphoric acid, bromine, manganese, alumina, and organic matter.

The bubbles of gas rising from the water in the basin contained 5·34 per cent. of carbonic anhydride and 94·65 per cent. of nitrogen by volume.

The mud collected from the sides of the basin into which the water flowed was thoroughly washed and then dried. It contained the following percentages:—1·533 of arsenious acid, 0·005 of lead sulphate, and 55·534 of ferric oxide, together with traces of antimony, copper, zinc, and manganese. Supposing the arsenious acid to bear the same proportion to the ferric oxide in the water as it does in the mud, 10,000 parts of the water would contain 0·0013 part of arsenious acid.

The analysis was conducted according to Bunsen's method, and the actual weights of the precipitates obtained are given: the arsenic was estimated by Bunsen's new method as pentasulphide. F. C.

The Hot Spring at Bagnoles de l'Orne, and the Deposits Formed in the Conduits. By DELACHANAL (*Ann. Chim. Phys.* [5], **21**, 275—278).

Analysis of the Water (per litre).

SiO ₂ .	K ₂ SO ₄ .	Na ₂ SO ₄ .	NaCl.	CaSO ₄ .	Ca ₃ P ₂ O ₈ .	Al ₂ O ₃ + Fe ₂ O ₃ .
0·0182	0·0040	0·0151	0·0127	0·0035	0·0003	0·0017

The total residue per litre was 0·0628, the organic matter and loss being 0·0073. There were traces of lithium, magnesium, zinc, and lead present.

The water had a perfectly neutral reaction; iodine and arsenic could not be detected. The numbers obtained by the author differ from those obtained by Henry in 1868, the total solid residue at that time, for example, being 0·1309 per litre. The composition of the water has evidently changed.

Analysis of Deposit.

SiO ₂ .	PbO.	ZnO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SnO ₂ .	
10·7	14·1	1·3	53·3	17·6	2·3	= 99·3

C. H. B.

Results of the Norwegian North Sea Expedition. By L. SCHMELCK) *J. pr. Chem.* [2], **22**, 165—188).—1. Solid constituents of sea-water.

The Northern Arctic Ocean has a mean sp. gr. of 1·0265, and contains per cent.—

CaO.	MgO.	K ₂ O.	Cl.	SO ₃ .
0·0578	0·2203	0·0472	1·9320	0·2214.

The average amounts of salts occurring in the sea and the composition of the sea-salt are:—

	In sea-water. per cent.	In sea-salt. per cent.
Calcium carbonate	0·0020	0·057
Calcium sulphate	0·1395	4·00
Magnesium sulphate	0·2070	5·93
Magnesium chloride	0·3562	10·20
Potassium chloride.....	0·0747	2·14
Hydrogen sodium carbonate..	0·0166	0·476
Sodium chloride	2·682	76·84

F. L. T.

Organic Chemistry.

Derivatives of the Heptane from Pinus Sabiniana. By F. P. VENABLE (*Ber.*, 13, 1649—1652).—*Heptyl bromide* obtained from this heptane is a colourless liquid of sp. gr. 1.422 at 17.5°; it boils at 165—167°.

Heptyl iodide does not distil without decomposition under ordinary pressure. It boils at 98° under 50 mm. pressure.

Heptyl acetoacetate boils at 250—260°, and is converted into methyl ethyl ketone, $C_5H_{11}.CHMe.CH_2.COMe$, on saponification.

Heptyl malonate (b. p. 263—265°) is formed by the action of ethyl malonate, alcohol, heptyl bromide, and sodium. When saponified with potash and the solution treated with hydrochloric acid, it yields *heptylmalonic acid*, a crystalline mass (m. p. 97—98°), little soluble in water, readily so in alcohol, chloroform, or ether. The silver and barium salts are white precipitates insoluble in water and in alcohol.

Heptylacetic acid is obtained on heating the last-mentioned acid to 160°. It is a colourless liquid (b. p. 232°), insoluble in water, soluble in alcohol and ether. The silver compound is sparingly, the barium salt readily, soluble in water. O. H.

Fermentation of Glycerol. By F. HOPPE-SEYLER (*Bied. Centr.*, 1880, 621—622).—From a study of the products of the fermentation of glycerol, it appears probable that this fermentation depends on the formation and decomposition of lactic acid, as glycerol is decomposed into the same products as the latter. J. K. C.

Di- and Tri-carbinols. By H. KOLBE (*J. pr. Chem.* [2], 22, 147—165).—The author is of opinion that as primary, secondary, and tertiary carbinols correspond to primary, secondary, and tertiary amines, so di- and tri-carbinols will be found corresponding to di- and tri-amines. For instance, ethylenediamine, $C_2H_4(NH_2)_2$, will have a corresponding ethylenedicarbinol, $C_2H_4(CH_2.OH)_2$; these di- and tri-carbinols can of course be primary, secondary, and tertiary in exactly the same manner as the di- and tri-amines are.

The primary di- and tri-carbinols, like the primary mono-carbinols, will be oxidisable to aldehydes and to acids. Only one of the aldehydes of the primary dicarbinols is known, that from ethylenedicarbinol corresponding with succinic acid. On the other hand, a large number of the corresponding bibasic acids are known. Succinic acid, for example, is the acid corresponding with ethylenedicarbinol; the alcohols belonging to malic, tartaric, and pyrotartaric acids are not yet known.

The secondary di- and tri-carbinols, like the secondary mono-carbinols, will only yield ketones on oxidation. Of the ketones of the secondary dicarbinols, our knowledge is very scanty. The compound called anthraquinone (which has nothing in common with the real quinones but a similarity in the empirical formula) belongs to this class, and may be regarded as the ketone of phthalic acid.

When reducing agents are discovered capable directly of removing oxygen from the alcohols, as many hydrocarbons can be prepared as we now know alcohols. Then will be produced :—

From methyl alcohol, MeOH , the hydrocarbon	MeH .
„ dimethylcarbinol, $\text{Me}_2\text{CH.OH}$, the hydrocarbon ..	$\text{CH}_2(\text{Me})_2$.
„ methylenedicarbinol, $\text{CH}_2(\text{CH}_2.\text{OH})_2$, the hydro- carbon	$\text{CH}_2(\text{CH}_3)_2$
„ methintricarbinol, $\text{CH}(\text{CH}_2.\text{OH})_3$, the hydrocarbon	$\text{CH}(\text{CH}_3)_3$
„ trimethintricarbinol, $(\text{CH})_3(\text{COH})_3$, the hydro- carbon	$(\text{CH})_3(\text{CH})_3$

This last hydrocarbon, trimethintrimethane, has the constitution of benzene. The same representation of the constitution of benzene is thus arrived at by comparison of the carbinols with their corresponding paraffins as arrived at by the author twelve years ago, on other grounds.

Pyrogallol (trimethintricarbinol) may be regarded as a tertiary alcohol, standing in the same relation to benzene as trimethylcarbinol to trimethylmethane. It cannot be denied that it differs in its properties from trimethylcarbinol, but nevertheless scarcely more than tribasic tricarballylic acid differs from monobasic butyric acid.

From the relations between benzene, phenol, and pyrogallol, it may be inferred that not only dimethintricarbinol, $(\text{CH})_2(\text{CH.OH})_3$, but also the compounds $(\text{CH})_2(\text{CH.OH})_2\text{CH}_2$, $(\text{CH})_2(\text{CH.OH})(\text{CH}_2)_2$, analogous to phenol, may be formed by the oxidation of dimethintrimethane, $(\text{CH})_2(\text{CH}_2)_3$.

The author remarks, that when in 1858 he foretold the existence of secondary and tertiary alcohols, the majority of chemists were still firmly attached to the type theory, and disbelieved in the possibility of the existence of such compounds. In the same way at the present time, the belief in “structure” and “bonds” prevents chemists from comprehending how secondary and tertiary di- and tri-carbinols can exist.

F. L. T.

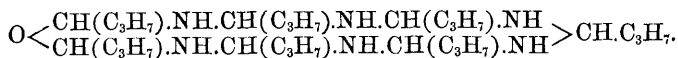
Methylamine in Commercial Trimethylamine Hydrochloride. By L. J. FISENBERG (*Annalen*, 205, 139—144).—The first portion of this paper is a brief summary of the literature of trimethylamine and its various sources. The author purified the commercial trimethylamine hydrochloride from ammonium chloride by evaporating to dryness, and taking up the residue with alcohol and ether; on evaporating the latter, the syrupy residue was decomposed by potash, and the vapour (b. p. 53°) passed into hydrochloric acid. The solution of the hydrochloride was mixed with excess of platinic chloride, the platinochloride washed with absolute alcohol and evaporated over sulphuric acid. The platinochloride gave on analysis 36.5 per cent. platinum (theory requires 37.4 per cent.). On frequent boiling of the platinum salt with alcohol the percentage of platinum increased after each operation. The identity of the platinochloride with that obtained by Hofmann from trimethylamine (obtained from herring brine) is confirmed by crystal measurements. From the analyses of the platino-

chloride and the percentage of chlorine in the hydrochloride, the author concludes that commercial trimethylamine hydrochloride contains methylamine; the latter may be separated from the former by washing with absolute alcohol. It appears that the solubilities of the platinochloride of mono-, di-, and tri-methylamine in water are inverse to their solubilities in alcohol. The author believes that he has obtained an alum of methylamine. V. H. V.

Some Derivatives of Isobutaldehyde. By A. LIPP (*Annalen*, **205**, 1—32).—As aldehydes undergo reactions with ammonia, varying according to the nature of the groups directly associated with the aldehydic group CHO, the author was induced to study this reaction, and that of hydrogen cyanide on the compound produced in the case of an aldehyde containing a (CH)^{'''} group. For this purpose isobutaldehyde was chosen as typical.

When ammonia gas is passed into an ethereal solution of isobutaldehyde, water is gradually formed, and on evaporation of the ether glistening crystals belonging to the hexagonal system separate out (see also this Journal, 1880, Abstr., 611). The substance has the empirical formula $C_{28}H_{62}ON_6$, and is formed according to the equation $7C_4H_8O + 6NH_3 = (C_4H_8)_7ON_6H_6 + 6H_2O$. The same compound may be obtained by using a strong ammoniacal solution instead of the gas. The crystals melt at 31° , and begin to decompose at 90° , with evolution of ammonia; they are with difficulty soluble in water, easily soluble in alcohol and ether. On heating the substance to 145° , a thick oily liquid, $C_6H_{15}O$, isomeric but not identical with conine, distils over ($C_{28}H_{62}N_6O = 3C_8H_{15}N + C_4H_8O + 3NH_3$).

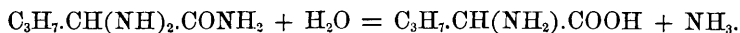
Action of Hydrogen Cyanide on the Isobutaldehyde Ammonic Compound.—By the action of a 30 per cent. solution of hydrogen cyanide, besides amidoisovaleronitril (Pfeffer, *Ber.*, **5**, 699), hydroxyisovaleronitril is produced $(C_4H_8)_7ON_6H_6 + 7HCN = 6C_4H_8NH_2CN + C_4H_8O.HCN$. At the same time, part of the amidoisovaleronitril is decomposed into ammonia and imidoisovaleronitril. By heating the products of the reaction with a 5 per cent. hydrochloric acid solution, the hydrochloride of the amidonitril is formed, which may be separated by its insolubility in ether from the unaltered imido- α -hydroxynitrils. On saturating the residue with ammonia, the free amidonitril becomes soluble in ether. The solution is dried over calcium chloride and saturated at 0° with dry hydrochloric acid, when the hydrochloride of amidoisovaleronitril is deposited. The author attributes to the compound of ammonia with isobutaldehyde the following formula:—



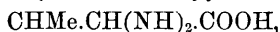
Hydrochloride of amidoisovaleronitril, $C_3H_7.CH(CN).NH_2.HCl$ is a white crystalline powder insoluble in ether, easily soluble in water and in absolute alcohol. It volatilises without melting; and with platinic chloride it forms golden scales of the platinochloride. By saturating an aqueous solution of the hydrochloride with ammonia, and extracting with ether, the free base, $C_3H_7.CH(CN).NH_2$, is obtained as a yellow oil of strongly alkaline reaction. By standing over sulphuric

acid it is gradually decomposed with formation of the corresponding imidonitril.

Hydrochloride of amidoisovaleramide, $C_3H_7.CH(NH_2.HCl).CONH_2$, is obtained by the action of fuming hydrochloric acid at ordinary temperatures on the hydrochloride of the amidonitril. It crystallises in plates of the monosymmetrical system, easily soluble in water, sparingly soluble in alcohol, insoluble in ether. The aqueous solution has a strongly acid reaction. It forms a platinochloride, which crystallises in the tetragonal system. By the action of silver oxide on the hydrochloride in water, amidoisovaleramide is obtained in solution; it cannot, however, be isolated in the pure state, as it decomposes even in a vacuum with formation of amidoisovaleric acid,

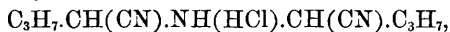


α-Amidoisovaleric acid (α-Amidoisobutylic acid),



is obtained by heating the hydrochloride of the amidonitril with hydrochloric acid of 1.1 sp. gr.; after separating the ammonium chloride by absolute alcohol, the hydrochloride of the amido-acid is decomposed with silver oxide. Thus obtained, amidoisovaleric acid forms a glistening crystalline mass; it dissolves easily in water, yielding a neutral solution, but is only sparingly soluble in alcohol, and insoluble in ether. It sublimes without melting. The acid is identical with that obtained by Clarke and Fittig from bromovaleric acid (*Annalen*, **139**, 200); and by Schmidt and Sachtleben from bromisobutylic acid (*ibid.*, **193**, 106; and this Journal, Abstr., 1879, 140). It forms salts with acids and bases. The hydrochloride can be obtained as an intermediate product of the reaction described above, or by the direct combination of the acid with hydrochloric acid. This substance is easily soluble in water and alcohol, the aqueous solution has a strongly acid reaction. The copper salt of amidoisovaleric acid forms blue scaly crystals.

Hydrochloride of imidoisovaleronitril,

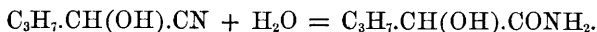


is obtained as one of the products of the action of hydrogen cyanide on the ammonia compound of isobutaldehyde (*vide supra*); it can be separated from hydroxyisovaleronitril by the insolubility of the hydrochloride in ether. It crystallises in prisms, and is easily soluble in alcohol, but is at the same time partially decomposed into hydrochloric acid and the imidonitril; this decomposition is effected immediately by water. It forms a platinochloride, which crystallises in golden needles.

Imidoisovaleronitril, $C_3H_7.CH(CN).NH.CH(CN).C_3H_7$.—By the action of ammonia on an ethereal solution of the hydrochloride, two isomeric imidoisovaleronitriles are obtained, one crystalline, the other an oily liquid. The solid isomeride melts at 52° . The hydrochlorides formed by the direct combination of hydrogen chloride with the two isomerides, are not distinguishable.

Hydroxyisovaleronitril, $CHMe_2.CH(OH).CN$, prepared by the direct combination of hydrogen cyanide with isobutaldehyde, $CHMe_2.CHO + HCN = CHMe_2.CH(OH).CN$ is a colourless oily liquid of sp. gr.

95612, which does not solidify even at -17° ; it is easily soluble in alcohol and ether. At 136° , it decomposes into hydrogen cyanide and the aldehyde. It dissolves in strong hydrochloric acid, taking up a molecule of water, and is converted into the corresponding amide,



α -Hydroxybutylformamide forms large scaly crystals (m. p. 104°), soluble in water and alcohol, sparingly soluble in ether; it distils unchanged. By heating with potash, ammonia is evolved, the amide is converted into *α -hydroxybutylformic acid*, $\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{COOH}$, identical with the acid obtained from bromvaleric acid by Clark and Fittig (*vide suprà*), and by Ley and Popoff (*Annalen*, **174**, 61), and by Schmidt and Sachtleben (*vide suprà*) from bromisobutylformic acid.

The acid may also be obtained by heating the corresponding nitril with concentrated hydrochloric acid; the ammonium chloride formed in the reaction may be separated by cooling after partial evaporation. On taking up with ether and evaporating, a dark coloured acid oil remains, from which, after standing a short time over sulphuric acid, needle-shaped crystals of the acid separate out. When pure, it crystallises in plates (m. p. 83°), belonging to the rhombic system; it is easily soluble in water, alcohol, and ether. By heating for some time with dilute sulphuric or hydrochloric acid (1 : 3), it is decomposed into formic acid and isobutaldehyde.

The calcium salt $(\text{C}_5\text{H}_9\text{O}_3)_2\text{Ca} + 4\text{H}_2\text{O}$, is prepared by neutralising the acid with chalk; it crystallises in needles. When air-dried, it gives up $2\frac{1}{2}$ mols. H_2O , the remainder at 100 — 150° .

The magnesium salt $(\text{C}_5\text{H}_9\text{O}_3)_2\text{Mg} + 2\text{H}_2\text{O}$, crystallises in prisms; it loses its water at 100 — 150° . A hydrated zinc salt $(\text{C}_5\text{H}_9\text{O}_3)_2\text{Zn} + 2\text{H}_2\text{O}$, is obtained by evaporating the aqueous solution over sulphuric acid; on drying it in the air, an anhydrous zinc salt, $(\text{C}_5\text{H}_9\text{O}_3)_2\text{Zn}$, is formed.

A copper salt, $(\text{C}_5\text{H}_9\text{O}_3)_2\text{Cu} + \text{H}_2\text{O}$, was also obtained. The salts in their solubility and other properties resemble those of hydroxyvalerianic acid obtained by Clark and Fittig. V. H. V.

Lead Formate Acetate. By J. PLÖCHL (*Ber.*, **13**, 1645—1647).—To the three double salts of the lower members of the acetic acid series, recently described by A. Fitz (*Ber.*, **13**, 1315; this Journal, Abstr. 1880, p. 799), the author adds a fourth, obtained in the form of needles, readily soluble in water, sparingly in alcohol, of the formula $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2\cdot\text{CHO}_2) + 2\text{H}_2\text{O}$.

It is impossible to separate acetic from formic acid by means of the solubility in alcohol of their lead salts, as stated in many works on the subject, because the formate passes into alcoholic solution together with the acetate.

The author contradicts the usual statement that 1 part of lead acetate is soluble in about 8 parts of strong alcohol. He found that 15—16 parts of 80 per cent. alcohol was required to dissolve 1 part of the salt. O. H.

Amido-acids of α -Hydroxybutyric Acid. By E. DUVILLIER (*Ann. Chim. Phys.* [5], **20**, 185—206).—Many years ago Volhardt showed that the synthesis of sarcosine or methyl-amido-acetic acid could be effected by the action of methylamine on ethyl chloracetate; by a similar reaction the author has prepared *methylamidobutyric acid*.

Normal α -bromobutyric acid is carefully added to a very concentrated solution of methylamine (prepared from dimethyl-oxamide), and the mixture heated in a closed vessel at 100 for several hours. When the action is complete, the product is boiled with baryta as long as methylamine is disengaged, and the excess of baryta is afterwards precipitated by dilute sulphuric acid. The filtrate, on being evaporated on a water-bath and allowed to cool, solidifies to a mass of slender needles, consisting of the hydrobromide of methylamido-butyric acid.

In order to purify the salt, it is dissolved in water; silver carbonate added to remove the hydrobromic acid, and the filtrate evaporated to dryness. The residue, dissolved in alcohol and crystallised, furnishes perfectly pure methylamido-butyric acid.

The results obtained by the analysis of this substance corresponded accurately with the formula $C_5H_{11}NO_2$, the constitutional formula of which may be written $CH_3.CH_2.CH(NHMe).COOH$.

The acid is very soluble in water and in boiling alcohol, but is insoluble in ether. It has a slightly sweet taste and a weak acid reaction. It may be heated to 120° without alteration, but at a higher temperature it is decomposed.

The aurochloride and platinochloride, hydrochloride, sulphate, nitrate, and the copper salt of methylamidobutyric acid were prepared and analysed. They present no characteristics of special interest.

Ethylamidobutyric acid, $CH_3.CH_2.CH(NHEt).COOH$, is prepared from ethylamine and bromobutyric acid by a process exactly similar to that described above in the case of the methyl compound. It is a crystalline substance, neutral to litmus, which can scarcely be distinguished from its lower homologue by any reaction. Its salts are strictly analogous to those already mentioned.

By treating bromobutyric acid with an ethereal solution of aniline, *phenylamidobutyric acid*, $CH_3.CH_2.CH(NHPh).COOH$, is obtained. By crystallisation from water, in which it is very slightly soluble, it presents itself as a granular, white, very light powder. It is very soluble in wood spirit, alcohol, and ether, and these solutions, like the aqueous, have a feeble acid reaction. It differs from methyl- and ethyl-amidobutyric acids, in that when warmed with solution of silver or mercurous nitrate, it produces a precipitate of metallic silver or mercury.

The hydrochloride is easily prepared by dissolving the acid in dilute hydrochloric acid, and allowing the solution to evaporate slowly in a vacuum; thus obtained, the salt forms groups of needles, which are very soluble in water, but much less so in alcohol and ether. The crystals of the hydrochloride rapidly become brown when exposed to light, and even in darkness, after the lapse of a certain time, they become perfectly black.

J. W.

Two Remarkable Cases of Metamerism in Carbon Compounds. By L. SCHREINER (*J. pr. Chem.* [2], **22**, 353—360).—The author has already described an easy method of making diethyl carbonate, $\text{CO}(\text{OEt})_2$ (*Annalen*, **197**), by slowly adding ethylchlorocarbonate (Cl.CO.OEt) to dilute sodium ethylate solution contained in a flask provided with a condenser.

This simple method has now been adopted by the author to prepare carbonates of the mixed alcohol radicals. Ethyl chlorocarbonate was first allowed to act on sodium methylate. After washing the product with water and drying it with calcium chloride, it was found to distil in greater part at 100° (730 mm. bar.), a small portion only coming over at 91° , and consisting of dimethyl carbonate. The larger portion, boiling at 104° , was proved by analysis and vapour-density determination to be methylethyl carbonate, EtO.CO.OMe .

By acting with methylchlorocarbonate on sodium ethylate, ethylmethyl carbonate was obtained. Dimethyl carbonate was prepared in a similar manner.

It was found that the methylethyl carbonate and ethylmethyl carbonate thus prepared are metameric bodies, a difference analogous to that already noticed between the corresponding glycollic compounds being observable. The differences are tabulated as follows:—

	Carbonates.		Glycollate.	
	B. p.	Sp. gr.	B. p.	Sp. gr.
Dimethyl	$91\cdot0^\circ$	1·0600	$134\cdot5^\circ$	1·0845
Methylethyl ..	$104\cdot0$	1·0372	$138\cdot6$	1·0746
Ethylmethyl ..	$115\cdot5$	1·0016	$142\cdot0$	1·0105
Diethyl	$125\cdot0$	0·9735	$158\cdot4$	0·9960

The author also obtained two metameric derivatives of urea, namely ethylmethylurea and methylethylurea. Ethylmethylurea was prepared by heating at 200° in a sealed tube a mixture of ethylic ethylamidoformate (EtHN.CO.OEt) with a solution of methylamine in absolute alcohol. The substance was precipitated from the alcoholic solution by addition of ether, or after distillation of the alcohol, it was crystallised from its aqueous solution by evaporation over phosphoric anhydride. The crystals are deliquescent, and melt at 105° .

The metameric methylethylurea was prepared in a similar way from ethylic methylamido formate, MeHN.CO.OEt , and ethylamine. Its crystals were very similar to those of the metameric body, but melted at 75° .

After repeated fusion, each of these substances begins to fuse at 91° , and the fusion finishes at 112° . This is considered to be due to the change into MeHN.CO.OMe and EtHN.CO.OEt ; the latter being known to fuse at $112\cdot5^\circ$, and the former probably fusing at 92° .

The theoretical importance of the above facts will be evident. The metamerism of the pairs of compounds can only be explained by the assumption that the bonds of the carbon atom are not similar.

F. C.

Borocitrates. By E. SCHEIBE (*Pharm. J. Trans.* [3], **11**, 389—390).—The borocitrates are specially valuable as remedies for diseases

of the kidneys and for urinary calculi. Their solvent power for urates and phosphates is about twice that of lithium benzoate. Soon after administration, boric acid may be detected in the urine, where it occurs partly in the free and partly in the combined state. Schwartz (*Sitzungsbericht d. Dorpater Naturforscher Ges.*, 1879, 204) has shown that the acid magnesium borocitrates, especially those containing the least proportion of acid, are strong antiseptics against bacteria. The diborocitrates are the best adapted for therapeutic purposes.

Magnesium forms three borocitrates, all of which do not crystallise—

Magnesium triborocitrate	$(C_6H_5O_7)_2Mg_3.(B_3H_3O_6)_2$.
„ diborocitrate	$(C_6H_5O_7)_2Mg_2.(B_2H_2O_4)_2$.
„ monoborocitrate . .	$(C_6H_7O_7)_2Mg.BHO_2$.

The preparations generally used gave the following results on analysis:—

	$C_6H_5O_7$.	Mg.	$B(HO)_3$.
(1) ..	61.64	6.23	32.13
(2) ..	73.50	8.83	16.67

Lithium borocitrates are all easily soluble in water. They are—

Lithium triborocitrate	$C_6H_5Li_3O_7.B_3H_3O_6$.
„ diborocitrate	$C_6H_6Li_2O_7.B_2H_2O_4$.
„ monoborocitrate	$C_6H_7LiO_7.BHO_2$.

Sodium Borocitrates.—The three sodium salts are known, being prepared from the carbonate—

Sodium triborocitrate	$C_6H_5Na_3O_7.B_3H_3O_6$.
„ diborocitrate	$C_6H_6Na_2O_7.B_2H_2O_4$.
„ monoborocitrate	$C_6H_7NaO_7.BHO_2$.

Ammonium borocitrates in the moist state gradually decompose, but when dry are stable. Three exist, similar in composition to the sodium and lithium compounds.

Potassium Borocitrates.—The diborocitrate is crystalline, being the only one which crystallises well.

Iron Borocitrates.—Preparations have been made by dissolving ferric hydrate in solutions of the acid borocitrates. Two compounds prepared with sodium di- and mono-borocitrate contained 8 and 16 per cent. of iron respectively.
L. T. O'S.

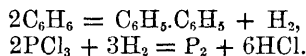
Constitution of Benzene. By J. THOMSEN (*Annalen*, 205, 133—138).—The author in another paper (*Ber.*, 13, 1388) has shown that the possible constitutional formulæ of benzene can be arranged in nine groups. Of these only two agree with the chemical characters of benzene (*i.e.*, the three isomeric tri-derivatives). These two are Kekulé's hexagon formula, with the alternate double and single bonds, and Ladenberg's formula with nine single bonds. The author proposes to decide between these formulæ by his theory of the heats of combustion and formation of the hydrocarbons, for by his researches he has shown that for single and double bonds an equal amount of energy is deve-

loped, whilst for a triple bond the energy developed is *nil*. This apparently extraordinary result can be explained thus. If the energy developed by the single bond be expressed by r , by the second affinity by *nil*, by the third by $-r$, then the double bond will give an energy of r , and a triple bond will give *nil*. This result is in perfect accordance with the chemical characters of the carbon compounds. In the case of the paraffins, in which all the carbon atoms are combined together by single affinities, and all the affinities of the carbon atoms are satisfied, the author has shown that the splitting off of each affinity is associated with a heat absorption of 14,570 heat-units. In the unsaturated compounds, in which two or more carbon atoms are combined together by a double or a triple bond, *these multiple bonds form the attacking point for chemical reagents*. For instance, when a molecule of chlorine acts on a molecule of ethylene, whereby the double bond of both carbon atoms is converted into two single bonds, the chlorine can combine with both carbon atoms with all the energy which corresponds to the affinity between chlorine and carbon. The conversion of the double bond into the two single bonds is not accompanied by an alteration of energy. In the case of acetylene, the conversion of the triple bond into a double and a single bond is associated with a development of energy in addition to that developed by the affinity of chlorine for carbon. But when chlorine acts on a paraffin, there must be a splitting off of a bond and an absorption of 14,570 heat-units, whether the reaction consists in the expulsion of a hydrogen atom or a dissociation into two hydrocarbon radicles. If the received hypothesis of benzene be correct, then the double bonds can be converted into single bonds by very violent reactions, whilst in all feeble reactions there will only be a substitution of the hydrogen atoms. The stability of benzene points to the absence of double bonds. According to the author's researches (*vide supra*), the heat developed in the formation of a hydrocarbon at constant volume can be expressed by a formula $(C_nH_{2m}) = -nd + (2m + x + y)r$, in which d is the dissociation-heat of carbon = 39,200 heat-units, x and y the number of single and double bonds, and r the heat-absorption in the combination of two carbon atoms, or one carbon atom and one hydrogen atom = 14,570 heat-units. For benzene, adopting Kekulé's hypothesis, we have $x = 3$, $y = 3$, $2m = 6$; for Ladenburg's hypothesis $x = 9$, $y = 0$, $2m = 6$, and the heat of formation of gaseous benzene at constant volume will be in the first case $-6 \times 39,200$ heat-units $+ 12 \times 14,570$ heat-units = $-60,360$ heat-units; in the second $-6 \times 39,200$ heat-units $+ 15 \times 14,570$ heat-units = $-16,650$ heat-units. The heat of formation of benzene at constant pressure is 1,160 heat-units greater, and the value above will become $-59,200$ or $-15,490$. If these values be subtracted from the heats of combustion of the constituents of benzene = 786,840, we have for the heat of combustion of benzene vapour, for the first hypothesis $786,840 + 59,200 = 846,040$ heat-units, and for the second $786,840 + 15,490 = 802,330$ heat-units. The experimental value found was 805,800 heat-units. The agreement between the experimental value and that theoretically deduced by adopting Ladenburg's hypothesis points to the conclusion that "*the six carbon atoms of benzene are combined together by nine single bonds,*

and the hypothesis adopted hitherto of a constitution of benzene with three single and three double bonds is not confirmed by experiment."

V. H. V.

Action of Phosphorus Trichloride on Benzene. By H. KÖHLER (*Ber.*, **13**, 1623—1625).—The author has examined the bye-products obtained when phosphenyl chloride is prepared, in the hope of finding diphenylphosphorus chloride or triphenylphosphine; but found that, besides the reaction $\text{PCl}_3 + \text{C}_6\text{H}_6 = \text{PCl}_2\text{C}_6\text{H}_5 + \text{HCl}$, only the following reactions took place, with production of diphenyl and phosphorus—



O. H.

Action of Sulphuric Acid on the Substituted Nitro- and Amido-benzenes. By J. POST (*Annalen*, **205**, 33—112).—The author briefly refers to the researches of Hübner, Ladenburg, Körner, and Nölting on the influence of a substituted element, or of a grouping on a second grouping introduced into the benzene nucleus. When nitrobenzene is converted into the nitrosulphonic acid, and this is reduced, there is formed a different body, or at least a mixture of isomerides differing from that obtained by the direct action of sulphuric acid on aniline (Meyer and Stüber, *Annalen*, **165**, 165; Limpricht, *ibid.*, **177**, 794; Post and Urlting, *Ber.*, **12**, 1460; this *Journal*, *Abst.*, 1880, 238).

On the other hand, the author has established that when a hydroxyl group is present, *i.e.*, when ortho- or para-, nitro- or amido-phenol is converted into the sulphonic acid, only one compound is produced. If the nitrophenolsulphonic acids are reduced, the same compound is obtained as when the corresponding amidophenols are converted into sulphonic acids (Brackebusch, *Ber.*, **7**, 163; Holst, *Ber.*, **13**, 617; *Abst.*, 1880, 642). According to the researches of Kolbe and Gaube (*Annalen*, **147**, 71) and Kekulé (*Zeits. f. Chem.*, 1867, 641), the same compound is obtained by nitrating paraphenolsulphonic acid and by converting orthonitrophenol into the sulphonic acid. The author by sulphating paranitrophenol and nitrating orthophenolsulphonic acid obtained the same compound (Post, *Ber.*, **6**, 395, and Stuckenberg, *Ber.*, **7**, 1322 and 1055). According to Nölting (*Monitscientif*, 680) these reactions can be attributed entirely to the presence of the hydroxyl grouping; accordingly the author has substituted bromine for the hydroxyl grouping, and has established that by sulphating orthamidobrombenzene, and by sulphating and subsequently reducing orthobromnitrobenzene the same sulphobromamidobenzene is produced (*Ber.*, **8**, 1557), although it has not yet been settled whether the same hydrogen atom is replaced by the sulphonic group. Hübner explains these reactions by supposing that when an amido-group is sulphated, the NH_2 group, by its combination with sulphuric acid, acquires negative properties, and acts like the negative nitro-group. To test this, the author has repeated Meyer, Strubner, and Limpricht's experiments (*vide supra*). In order to establish which hydrogen atom is replaced by the sulphonic group, the author has investigated the influence of the presence of a second amido-group by nitrating their

benzoyl derivatives, and subsequently removing the benzoyl groups. But these researches are incomplete, owing to the easy decomposition of the complex benzoyl derivatives (Stuckenberg, *Ber.*, **7**, 1322, and **10**, 380—385).

In order to decide between the isomerism or identity of the amidophenolsulphonic acid from the nitrophenol, the author has studied the reaction of bromine and iodine on the paranitrophenolsulphonic acid, and investigated the iodo- and bromo-nitrophenolsulphonic acid, and diiodo- and dibromo-nitrophenols formed in the reactions (Brackebusch, *Ber.*, **7**, 167). These compounds were isomeric with those obtained by Armstrong and Brown (this Journal, **25**, 859) by the action of bromine and iodine, on nitrophenolsulphonic acid from orthonitrophenol.

Sulphating Paranitrophenol (m. p. 115°). By J. POST (see also *Ber.*, **6**, 395).—In this paper the only new chemical matter is the correction of molecules of water of crystallisation of the barium salt of the paranitrophenolsulphonic acid: in the former communication in the *Berichte* the author attributed to the barium salt the formula $C_6H_3(NO_2).SO_3.O.BaH_2O$, in this paper the author alters the formula to $C_6H_3(NO_2).SO_3O.Ba_2H_2O$.

Comparison of the salts of the nitrophenolsulphonic acid $[OH : SO_3H : NO_2 = 1 : 2 : 4]$:—

	Körner.		Post. Neutral.
	Acid.	Neutral.	
Potassium salt	—	H ₂ O	—
Sodium	2H ₂ O	2H ₂ O	2H ₂ O
Calcium	3H ₂ O	H ₂ O	2½H ₂ O
Barium	H ₂ O	H ₂ O	2H ₂ O
Copper	—	—	anhyd.
Lead	—	—	1½H ₂ O.

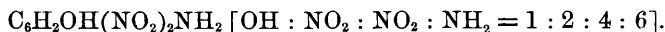
Nitrating Orthophenolsulphonic acid. By C. STUCKENBERG (also *Ber.*, **7**, 1332, and **10**, 55; this Journal, Abst., 1877, ii, 888).

Amidophenolsulphonic acids. By J. POST (also *Ber.*, **6**, 395).

Proof of the Identity and Isomerism of the various Amidophenolsulphonic acids. By F. BRACKEBUSCH (also *Ber.*, **7**, 163, and L. HOLST, *Ber.*, **13**, 617; this Journal, Abst., 1880, 642).

Conversion of Orthophenolsulphonic acid into the Para-compound. By J. POST (also *Ber.*, **8**, 1547; this Journal, 1876, i, 579).

Orthonitramido- and Orthodiamido-phenols and their Nitro-substitution Products. By C. STUCKENBERG (also *Ber.*, **7**, 1322, and **10**, 380—385; Abst., 1877, ii, 193).—In this paper the only new chemical fact is the proof of the identity of the amidodinitrophenol $[OH : NH_2 : NO_2 : NO_2 \text{ or } OH : NO_2 : NH_2 : NO_2 = 1 : 2 : 4 : x]$, obtained by nitrating the monobenzoyl derivative of paramidonitrophenol $[OH : NH_2 : NO_2 \text{ or } OH : NO_2 : NH_2 = 1 : 2 : 4]$, and subsequently removing the benzoyl group with picramic acid,



This shows that the author's paramidonitrophenol had the constitution $OH : NO_2 : NH_2 = 1 : 4 : 6$.

Introduction of Bromine and Iodine into Nitrophenolsulphonic Acid [OH : SO₃H : NO₂ = 1 : 2 : 4]. By F. BRACKEBUSCH (also *Ber.*, **7**, 167).

Sulphonic Acids from Nitramido- and Diamido-benzenes in Ortho- and Meta-Series. By J. POST and E. HARDTUNG (also *Ber.*, **13**, 38; *Abst.*, 1880, 394).

Formation of Amidosulphobenzenes from Nitrobenzene and Aniline. By L. WITTING and J. POST (also *Ber.*, **12**, 1460; *Abst.*, 1880, 238).

V. H. V.

Oxidation of Nitrogenous Methylated Benzene Derivatives.

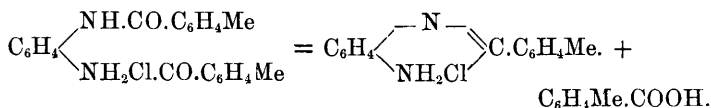
By A. BRÜCKNER (*Annalen*, **205**, 113—133).—PART I. *Anhydro-*

benzamidoparatoluic Acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C.C}_6\text{H}_4.\text{COOH}$ [NH : N = 1 : 2],

[C : CCOH = 1 : 4].—Anhydrotolyldiamidobenzene was prepared either by the action of paratoluic chloride on orthonitraniline, and reducing the tolylnitranilide formed (Stover's process, *Ber.*, **7**, 463, 1314), or by the direct action of orthodiamidobenzene on paratoluic chloride. This latter reaction is so violent that it must be moderated by the addition of benzene. After evaporation, a mixture of a neutral and a basic substance is left. The neutral compound may be separated by solution in acetic acid, and precipitating with water; it forms colourless needles (m. p. 228°), and is most probably the diparatoluide of orthodiamidobenzene, $\text{C}_6\text{H}_4(\text{NHCO.C}_6\text{H}_4\text{Me})_2$. The basic substance is precipitated from the acetic acid solution by sodium carbonate, and is converted into the hydrochloride by hydro-

chloric acid. It has the formula $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C.C}_6\text{H}_4\text{Me}$ [C : Me = 1 : 4],

and belongs to the class of anhydro-bases. The author shows that its production in the reaction above is due to the decomposition of the hydrochloride of the toluidide into the anhydro-base and paratoluic acid—



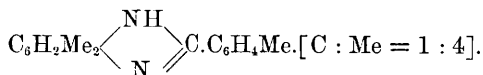
The base separates out in golden flocks (m. p. 268°); its nitrate and sulphate crystallise in long needles.

In order to obtain anhydrobenzamidoparatoluic acid, the anhydro-base is oxidised with chromic acid mixture, precipitated with excess of water, and the acid purified from the unoxidised base by converting it into its ammonium salt. Its melting point lies above 300°; it crystallises from water with $1\frac{1}{2}\text{OH}_2$, and from alcohol with 2HO_2 . A very soluble potassium salt, crystallising in glistening needles, and sparingly soluble barium and calcium salts are described. The silver salt is an insoluble precipitate, from which may be prepared the corresponding ethyl salt (m. p. 242°), crystallising in slender needles.

Anhydrotolylketamine, $(\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C.C}_6\text{H}_4)_2\text{CO}$.—The silver salt of

anhydrobenzamidotoluic acid when heated in a sealed tube is decomposed; on exhausting the crude product of the reaction with alcohol, and evaporating the solution, crystalline needles (m. p. 277°) of anhydrotolylketamine separate out. A hydrochloride of this base, crystallising in long needles, and a platinochloride, are described.

PART II. *Oxidation of Anhydrodiamidoparatolylxylene,*



Xylidine and paratoluic chloride react to form a hard compact mass, which is best purified by dissolving the crude product in alcohol, precipitating with water, and separating the filtrate by distillation in a current of steam. The residue is purified by crystallising out from alcohol. Paratolylxylidine forms long colourless needles (m. p. 137°), insoluble in water, soluble in alcohol and acetic acid. By directly nitrating paratolylxylidine with fuming nitric acid, some higher nitro-compound is formed. The mononitro-derivative can be prepared by the action of fuming nitric acid on an acetic acid solution of paratolylxylidine. It forms golden needles (m. p. 187°). By reducing mononitroparatolylxylidine, it is converted into anhydroparatolylidiamidoxylene. The base forms colourless crystals (m. p. 217°); its sulphate, chloride, and nitrate are described. By its oxidation, an acid, soluble in alcohol, was obtained, but in quantity too small for a minute examination.

PART III. *Oxidation of Benzotoluidine.*—Benzoparatoluidide is prepared by the direct action of benzoic chloride on paratoluidine; the product is dissolved in concentrated acetic acid, and oxidised with excess of chromic acid. The acetic acid solution is precipitated with water, and the precipitated acid purified from the unoxidised toluidide by solution in soda.

Benzoparamidobenzoic acid, $\text{C}_6\text{H}_4(\text{COOH}) \cdot \text{NH}\bar{\text{B}}\text{z} [\text{COOH} : \text{NH}\bar{\text{B}}\text{z} = 1 : 4]$, thus prepared, forms stellate groups of needles (m. p. 278°), sparingly soluble in hot water, soluble in alcohol, ether, and acetic acid. The copper salt is insoluble, the silver salt forms pearly glistening needles; the barium and calcium salts are also described. By heating with dilute sulphuric acid at 150—170°, it is decomposed into benzoic and paramidobenzoic acids.

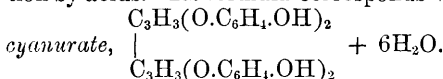
Benzorthamidobenzoic acid, $\text{C}_6\text{H}_4(\text{COOH}) \cdot \text{NH}\bar{\text{B}}\text{z} [\text{COOH} : \text{NH}\bar{\text{B}}\text{z} = 1 : 2]$.—Benzorthotoluidide prepared by a process analogous to the para-compound crystallises in glassy needles (m. p. 142°), insoluble in cold, soluble in hot water. The orthotoluidide when oxidised with chromic acid gave negative results; by heating with alkaline permanganate, it is converted into benzorthamidobenzoic acid. It crystallises in needles (m. p. 182°), insoluble in water, soluble in alcohol and ether. The barium and calcium salts crystallise with $8\text{H}_2\text{O}$, and the magnesium and sodium salts with $4\text{H}_2\text{O}$. An acid identical with this was obtained from orthoamidobenzoic acid by the direct replacement of the hydrogen atom in the amido grouping by benzoyl.

PART IV. *Oxidation of paratolylanilide,*

Paratoluic chloride and aniline act violently on one another; the purified anilide crystallises in white needles (m. p. 140–141°), sparingly soluble in water, soluble in acetic acid. The preparation of the corresponding acid by oxidation with alkaline permanganate was a failure, nothing but terephthalic acid being produced. V. H. V.

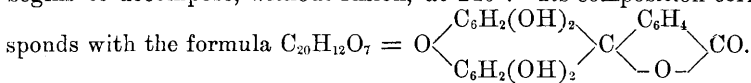
Some Constituents of the Essential Oil of *Origanum Vulgare* and *Thymus Serpyllum*. By E. JAHNS (*Arch. Pharm.* [3], 16, 277–280).—The essential oil of *Origanum vulgare* is shown to contain the same phenols (carvacrol principally) that are present in *O. hirtum* and *O. smyrnæum*, although in very small quantities. The oil of *Thymus serpyllum* contains three phenols, one having a smell of creosote, the other two, which are removed by ether from the potash solution of crude phenols, are thymol and carvacrol. Great difficulty was experienced in obtaining the carvacrol in a solid form, as the presence of a small quantity of thymol lowers its melting point to –17°. Artificial and natural carvacrol are identical, the only difference between the two up to the present time having been that the natural substance gave a reaction with ferric chloride, whereas the artificially prepared carvacrol gave no reaction. This is shown to be due to the solvent, for when both are dissolved in alcohol, the reaction is similar in both cases. E. W. P.

Action of Resorcinol on Urea. By K. BIRNBAUM and G. LURIE (*Ber.*, 13, 1618–1621).—When a mixture of 1 part of resorcinol with 2 of urea is heated at 250°, until evolution of gas has ceased, a crystalline reddish-brown residue remains, insoluble in water, alcohol, ether, and in the usual solvents, soluble with difficulty in glacial acetic acid, readily soluble in ammonia and in alkali, and precipitated from its solution by acids. Its formula corresponds with that of *dihydroxyphenylene cyanurate*,



Cyanuric acid heated with resorcinol at 250° yields the same compound. O. H.

Phloroglucolphthaleïn and Diresorcinolphthaleïn. By G. LINK (*Ber.*, 13, 1652–1656).—The former of these phthaleïns, obtained by a process analogous to that by which A. Baeyer prepared fluoresceïn, forms reddish-brown microscopic needles, soluble in alkalis without fluorescence, and in water, alcohol, ether, and acetic acid; it is insoluble in benzene, chloroform, and carbon bisulphide. When heated, it begins to decompose, without fusion, at 240°. Its composition corre-



Dissolved in soda solution and treated with zinc-dust, it yields the corresponding phthalin, in the form of a thick brown oil, becoming

solid on prolonged drying; it could not be obtained in a crystallised condition, however.

Diresorcinolphthaleïn is formed on fusing diresorcinolphthalic anhydride and stannic chloride. It forms silvery laminæ or needles, containing $5\frac{1}{2}$ mols. H_2O , which are soluble in alkalis with a blue, and in concentrated sulphuric acid with a brown coloration. It decomposes at 245° , without fusing.

The corresponding *phthalin* crystallises in colourless laminæ, containing $8\frac{1}{2}$ H_2O ; it melts at 238° , with partial decomposition. O. H.

Some Derivatives of Isophthalic Acid. By B. BEYER (*J. pr. Chem.* [2], 22, 351—352).—A quantity of isophthalic acid, prepared by Fittig's process, was converted in part into chloride by heating with phosphorus pentachloride, and the chloride was converted into amide by careful addition to aqueous ammonia solution. The amide is a light white powder (m. p. 265°), slightly soluble in boiling alcohol, and almost undissolved by the other usual solvents. When heated with phosphoric anhydride, it yields metadiacyanbenzene (m. p. 156°).

The nitro-isophthalic acids were made by treating the acid with fuming nitric acid; one of them crystallising in scales was that described by Fittig (m. p. 249°); but an isomeric acid crystallising in small needles was also obtained (m. p. 260°).

These derivatives of isophthalic acid were identified by a nitrogen determination in each. The author intends to examine them fully.

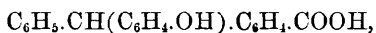
F. C.

Preparation of Orcinolcarboxylic Acid (Pseudorcellic Acid). By H. SCHWARZ (*Ber.*, 13, 1643—1645).—By a method identical with that for the preparation of salicylic acid by Kolbe and v. Heyden, the author obtained from orcinol, orcinolcarboxylic acid identical with that produced by Senhofer and Brunner (*Wien. Akad. Ber.*, 1880) by a different method. It is very readily soluble in alcohol and ether; with difficulty in water, from which it crystallises in long white needles. Heated to fusion, carbonic anhydride is evolved, and orcinol is reformed, readily recognisable by the green fluorescence when heated with alkali and chloroform. This pseudorcellic acid, unlike ordinary orcellic acid, does not yield an ethereal salt when boiled with alcohol. O. H.

Compounds of Orthobenzoylbenzoic Acid with Phenols. By H. v. PECHMANN (*Ber.*, 13, 1608—1618).—*Monoxydiphenylphthaleïn*, formed on heating benzoylbenzoic acid with phenol and stannic chloride, crystallises from ether in colourless crystals (m. p. 155°), soluble in all ordinary solvents, excepting water and light petroleum. It dissolves in alkalis with a violet colour, similar to that produced by phenolphthaleïn.

Acetylmonoxydiphenylphthaleïn is obtained as a crystalline mass (m. p. 135 — 136°), on heating the former compound with acetic anhydride and sodium acetate. It yields a dibromo-compound (m. p. 196°) on bromination.

Monoxydiphenylmethanecarboxylic acid,



is obtained in colourless, shining crystals (m. p. 210°) by reducing the oxydiphenylphthalein with zinc-dust.

Monoxyphenylanthranol is formed on treating the phthalein with concentrated sulphuric acid, but could not be obtained in a crystallised state. By oxidation with sodium manganate, an oxanthranol was obtained, which was converted into the corresponding acetyl-derivative, crystallising in needles (m. p. $207-270^{\circ}$). O. H.

Vulpic Acid. By A. SPIEGEL (*Ber.* **13**, 1629—1635).—The author has investigated this acid, which has recently been studied by Möller and Strecker (*Annalen*, **113**, 56). He obtained from *Cetraria vulpina*, collected at Pontresina, in Switzerland, 1.5—2 per cent. of the acid, from the Scandinavian plant about 4 per cent. It melts at 148° , and when heated to 200° splits up into methyl alcohol and *pulvic anhydride*, $C_{18}H_{10}O_4$, which crystallises from benzene in the form of light yellow needles (m. p. $120-121^{\circ}$), is but slightly soluble in alcohol, more readily in hot chloroform, benzene, glacial acetic acid and acetone, insoluble in water or in alkaline carbonates. It sublimes unchanged when carefully heated. When heated with soda solution and acetone, it dissolves, and the addition of hydrochloric acid to the solution throws down *pulvic acid*, $C_{18}H_{12}O_5$ (m. p. $214-215^{\circ}$). The same acid is obtained from vulpic acid by heating it with milk of lime and acidulating the solution. It is readily soluble in alcohol, less so in chloroform, ether, or acetic acid, and in water.

Acid silver pulvate crystallises in tufts of yellow prisms. *Neutral silver pulvate* crystallises in long needles. *Barium pulvate* forms bright yellow laminae, sparingly soluble in water. *Calcium pulvate* crystallises in long yellow needles, and *copper pulvate* in dark blue needles. The *alkaline pulvates* are very soluble, and crystallise with difficulty.

The potassium salt of *ethylpulvic acid* is obtained on adding *pulvic anhydride* to alcoholic potash. The free acid crystallises from alcohol in transparent yellow tablets (m. p. $127-128^{\circ}$). When heated, it decomposes, with formation of ethyl alcohol.

Methylpulvic acid is identical with vulpic acid.

The formation of an acid ether in alkaline solution by the mere addition of an alcohol to an anhydride is without parallel, but resembles the direct formation of the ethers of orsellic acid.

Pulvamic acid, $C_{18}H_{13}NO_3$, formed by adding ammonia to *pulvic anhydride*, crystallises from benzene in monoclinic yellow prisms (m. p. 220°). It is soluble in ordinary solvents, insoluble in water and mineral acids; unaltered by nitrous acid.

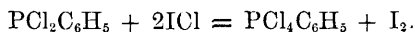
Dimethyl pulvate melts at $138-139^{\circ}$.

Methyl acetylulvate, $C_{18}H_{10}O_5 \cdot \text{AcMe}$, obtained by treating vulpic acid with acetic anhydride, crystallises from alcohol in long silky needles (m. p. 156°), insoluble in soda solution.

Well crystallised derivatives of vulpic acid are formed on treating its ammoniacal solution with zinc-dust. O. H.

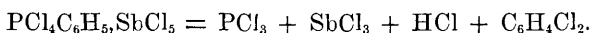
Action of Phosphenyl Dichloride on some Chlorides. By H. KÖHLER (*Ber.*, **13**, 1626—1629).—Iodine monochloride acts violently

on phosphenyl chloride, free iodine separates, and phosphenyl tetrachloride is produced—



Neither tin chloride nor silicium chloride acts on the phosphenyl chloride.

Titanic chloride yields the compound $\text{PCl}_4\text{C}_6\text{H}_5$. Antimony trichloride mixes with the phosphenyl chloride in all proportions, without formation of a definite chemical compound. The pentachloride, however, is readily acted on, with the formation of *antimony phosphenyl superchloride*, $\text{PCl}_4\text{C}_6\text{H}_5\cdot\text{SbCl}_5$, a solid, hygroscopic substance, fuming when exposed to the air, and decomposing on heating with the production of *paradichlorobenzene*—



O. H.

Baeyer's Process for the Synthesis of Indigotin. By ROSENSTIEHL (*Ann. Chim. Phys.* [5], **21**, 286—288).—Baeyer has described two processes for the preparation of indigotin from cinnamic or phenylacrylic acid: this is first converted into ortho-nitro-cinnamic acid by the usual method, the ortho-derivative being apparently the only one from which indigotin can be obtained. In one process, the ortho-nitro-cinnamic acid is converted (in the same way that cinnamic acid is transformed into phenyl-oxyacrylic acid) into ortho-nitro-phenyl-oxyacrylic acid, which when heated at 110° , swells up and gradually darkens in colour. When the product thus formed is treated with alcohol, an insoluble residue of indigotin remains, but the yield is only very small, and the decomposition is probably highly complicated.

The second process gives much better results. The ortho-nitro-cinnamic acid is converted by the action of bromine, and subsequent treatment with a boiling alcoholic solution of potash into ortho-nitro-phenyl-propionic acid, and when this acid is heated at 110° with a mixture of an alkali and a reducing agent, preferably a mixture of sodium carbonate and glucose, indigotin separates out in the crystalline form, $\text{C}_8\text{H}_5\text{NO}_4 + \text{H}_2\text{O} = \text{C}_8\text{H}_5\text{NO} + \text{CO}_2 + \text{H}_2\text{O}$.

If a fabric be impregnated with a mixture of the acid, glucose, and sodium carbonate, and heated to the required temperature, by means of superheated steam, for example, indigotin is formed, and is firmly fixed in the fibres of the cloth. The importance of this reaction in colour-printing is obvious.

It would appear that the phenyl group in the indigotin is capable of undergoing various substitutions, with production of colouring matters giving different shades of blue.

C. H. B.

New Hydrocarbon from Sequoia Gigantea. By G. LUNGE and T. STEINKAULER (*Ber.*, **13**, 1656—1658).—From the leaves of the Californian giant pine, *Sequoia gigantea*, the authors obtained white laminar crystals with bluish fluorescence (m. p. 105° ; b. p. $290-300^\circ$). This substance is very readily soluble in all ordinary solvents

except water, and has the formula $C_{13}H_{10}$. It is isomeric with fluorene, and the authors propose for it the term *sequoiene*.

Besides this substance, the leaves of the Sequoia yield three different oils, boiling respectively at 155° , 190 – 200° , and at 240° C.
O. H.

Combinations of Anthracene with the Oxides of Nitrogen.
C. LIEBERMANN and L. LINDEMANN (*Ber.*, **13**, 1584–1590).—Nitro-compounds of anthracene have not hitherto been obtained, because on treatment with nitric acid, anthracene at once yields anthraquinone and nitro-anthraquinones. By acting on anthracene dissolved in glacial acetic acid with nitrous acid vapours, the authors have obtained various additive products.

Anthracene Nitrate, $C_{14}H_{10}.NO_3H$.—A current of nitrous acid is passed into glacial acetic acid at 30° , in which anthracene is suspended; it dissolves, and crystals soon separate from the brown solution. These washed with alcohol and recrystallised from benzene, form white needles or prisms, melting, with decomposition, at 125° .

The compound, $C_{14}H_{10}.2NO_2$, is obtained if the temperature is not allowed to rise above 15° . The anthracene alters but little in appearance, but gradually becomes converted into the new compound. This may readily be separated from the anthracene by boiling with benzene, in which it is sparingly soluble; it may be purified by crystallisation from toluene. It is very sparingly soluble in alcohol, forms white laminae, fusing at 194° , and decomposing a few degrees above that point, leaving *nitrosoanthrone*, $C_{14}H_8NO_2$, or $C_6H_4 : CO.CH(NO) : C_6H_4$, the term *anthrone* being proposed for such anthracene derivatives as contain one of the carbon atoms of the central C_2 group in the form of carboxyl. Nitrosoanthrone is more readily obtained in the form of a yellow powder by heating the compound $C_{14}H_{10}.NO_3H$ with dilute alkali. It crystallises from alcohol in beautiful long yellow needles (m. p. 146°).

Nitrosohydranthrone, $C_{14}H_{11}NO_2$, is obtained in the form of a flesh-coloured precipitate on neutralising the alkaline filtrate from the nitrosoanthrone with acids, the liquid being kept cool.

Sodium nitrosohydranthrone, $C_{14}H_{10}NO_2Na$, separates on the addition of concentrated soda solution to an alkaline solution of the previous compound, as long yellow needles.

Nitrosoanthrone heated with alcoholic potash, or with tin and glacial acetic acid, is readily converted into the corresponding hydranthrone.

On oxidising the various nitro-compounds with chromic acid, pure anthraquinone is formed, proving that the nitrogen group is joined to the central C_2 group.

On heating a mixture of nitrosoanthrone and phosphorus pentachloride at 180° , a grey mass is produced, which after treatment with boiling alcohol and crystallisation from a mixture of light petroleum and benzene yields *dichloranthracene tetrachloride*, $C_{14}H_8Cl_6$, in the form of white needles (m. p. 205 – 207°). Treated with boiling alcoholic potash, it turns yellow, and yields *tetrachloranthracene*, $C_{14}H_6Cl_4$, very little soluble in alcohol, more so in boiling glacial

acetic acid, and crystallising in yellow needles (m. p. 152°). By oxidation with chromic acid, a well crystallised dichloranthraquinone is formed, giving an alizarin coloration on fusion with potash. The hydroxyanthraquinone produced has not yet been examined.

O. H.

Derivatives of Anthraquinone. By C. LIEBERMANN (*Ber.*, **13**, 1596—1603).—Experiments were undertaken to decide which of the two possible formulæ for anthraquinol, proposed by Gräbe and Lieber-

mann, was correct, $C_6H_4 \begin{array}{c} \text{CH(OH)} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} C_6H_4$ or $C_6H_4 \begin{array}{c} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{C(OH)} \end{array} C_6H_4$.

By acetylation, the monacetyl derivative was the only one that could be recognised with certainty, the existence of a diacetyl compound being doubtful.

Anthraquinol treated with excess of ethyl iodide, or amyl iodide, yields only mono-substitution derivatives.

Ethylxyanthrone, $C_6H_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OEt)} \end{array} C_6H_4$, crystallises in strongly refractive rhombic prisms (m. p. 106—107°): the alcoholic solution has a beautiful blue fluorescence. On heating the compound, it distils with loss of water.

Amyloxyanthrone forms shining colourless crystals. On treatment with fuming nitric acid, the ethyl derivative yields a dinitro-compound, $C_{14}H_6(NO_2)_2(OH).OEt$, and by reduction with hydriodic acid and red phosphorus, a hydrocarbon, $C_{16}H_{16}$, *ethylanthracene dihydride*, is produced, the amyloxyanthrone giving the corresponding hydride, $C_{19}H_{22}$. Both are colourless oily liquids of high boiling point. Both oxyanthrones dissolve in concentrated sulphuric acid, forming cherry-red solutions, from which water precipitates needles, dissolving in alcohol with magnificent green fluorescence.

The author concludes that the constitution of anthraquinol is represented by the formula, $C_6H_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OH)} \end{array} C_6H_4$.

O. H.

Reduction-products of Camphor. By H. SCHRÖTTER (*Ber.*, **13**, 1621—1623).—Camphor distilled over heated zinc-dust yields benzene, toluene, paraxylene, and cymene. Hence the products are identical with those obtained by the action of fused zinc chloride on camphor (Fittig, Koebrich, and Jilke, *Annalen*, **145**, 129). Instead of laurene, described by Fittig, the author obtained further a hydrocarbon boiling between 164—167°, and probably a pseudocumene.

O. H.

Coffee Oil. By C. O. CECHE (*J. pr. Chem.* [2], **22**, 395—398).—The author communicates some preliminary work on the subject of this oil. During the roasting of coffee berries, the odour of the oil is very apparent, and it may be seen on the surface of the concentrated extract of coffee in the form of small drops. The quantity of oil present varies according to the source and condition of the berries, being from 8—13 per cent., and of this at least one-half is volatilised during the process of roasting. No considerable escape of gas or oil vapour occurs

during the roasting until the berries turn brown. At that stage, the berries are turned out and tossed in the air so as to cool them very rapidly and prevent their burning; the oil vapour is thus lost, but might be saved by connecting the roasting drum with an exhaustor which would prevent the risk of the berries catching fire, and would render it possible to remove and condense the vapour of the oil. The oil thus obtained would doubtless be of value for liqueurs.

The preparation of the oil was carried out by extracting it from 50 lbs. of powdered coffee berries of various kinds by means of ether-alcohol. In this way about 1,200 grams of a green, transparent, thick oil were obtained. It deposited crystals of caffeine after standing for a time; and after three years separated into crystalline fatty acids, and a clear green layer of liquid oil, the crystals forming about two-thirds of the whole. F. C.

Palembang Benzoïn. By E. SAALFELD (*Arch. Pharm.* [3], 16, 280).—Palembang benzoïn from Sumatra is free from cinnamic acid, and gives a yield of 10 per cent. of benzoic acid. It is better adapted for preparing the tincture than the Siamese gum, as the colour of the tincture is lighter, has a fainter odour, and does not become milky when added to water, but is precipitated in flocks. E. W. P.

Light Resin Oil. By W. A. TILDEN (*Ber.*, 13, 1604—1607).—The distillate boiling under 80° consists chiefly of *isobutaldehyde*; between 103 — 104° a mixture of hydrocarbons distils; these partially polymerise on treatment with sulphuric acid diluted with 25 per cent. of water and an oil, boiling between 245 — 247° is obtained. Heated with sulphuric acid until sulphurous anhydride is evolved, a black liquid is obtained which yields an intensely green solution when diluted with alcohol, and soon deposits a green precipitate. The hydrocarbons left undissolved by dilute sulphuric acid, heated with a mixture of concentrated and fuming sulphuric acid, separate into a portion not acted on, consisting apparently of a heptane (b. p. 95 — 97° , sp. gr. at 15° 0.763), whilst the green sulphuric solution, on dilution with water, yields a black precipitate, probably of the empirical formula $C_{20}H_{28}O_3$. On oxidation with nitric acid this furnishes two acids, of which one readily crystallises; these have not yet been examined.

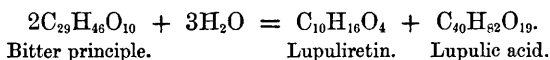
When the fraction distilling between 103 — 104° is shaken with water in contact with air, it yields the crystalline substance $C_{10}H_{24}O_4$, described by Tichborne (*Pharm. J. Trans.* [3], 1, 302).

The fractions of higher boiling point were free from toluene, but contained an optically inactive terpene. O. H.

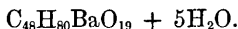
The Bitter Principle and Resin of Hops. By M. ISSLEIB (*Arch. Pharm.* [3], 16, 345—363).—The literature of the subject is first discussed, the discrepancies existing between the statements of the various authors are pointed out, the cause of these discrepancies being the imperfect methods employed for the separation of the various substances present in the hops. By the term "bitter principle" is to be understood substances which under the influence of boiling acids or alkalis, and sometimes ferments, break up into sugar and some other

substance, belonging then, as a rule, to the glucosides. They have for the most part a bitter taste, an acid or neutral reaction, and a few of them contain nitrogen. They differ from the alkaloids in not containing nitrogen and in their feeble action on the animal economy, picrotoxin, colchicin, and a few others being exceptions. At the same time as the author examined the extract of hops, he also examined the composition of "lupulin," which, according to Ives, is a yellow powder found at the base of the scales of the hop cones.

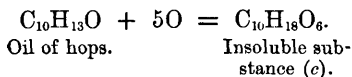
After a preliminary and comparative trial of the effects of hot and cold water, ether and alcohol, on both lupulin and hops, he proceeds to describe the method he has employed for the isolation of the bitter principle. An extract of hops with cold water was treated with animal charcoal, and the charcoal after careful drying was exhausted with 90 per cent. alcohol; the result was a yellow solution, which on partial evaporation yielded a precipitate of a brown resin (*a*), and in the solution a bitter substance remained which could not be crystallised. Ether removes from the aqueous solution of the above only the bitter principle (*b*), leaving another substance which is not bitter (*c*), dissolved in the water. The true "bitter" amounts to only 0.004 per cent. of the hops, whereas when lupulin is submitted to a like process the yield is 0.11 per cent. of the lupulin employed. The "bitter" (*b*), which is pale yellow, darkens at 60°, and if the temperature remains constant for some time it can be powdered; it is soluble in cold water, alcohol, benzene, &c., and is amorphous, non-nitrogenous, and slightly acid. Alkalis dissolve it with an intense yellow coloration, but no colour is produced by the addition of ferrous or ferric salts. From analysis, it would seem to be of the composition $C_{29}H_{46}O_{10}$, and under the influence of sulphuric acid it is decomposed into "lupulic" acid and "lupuliretin," thus:—



Of the properties of lupulic acid, no description is given, except that it is crystalline, as the quantity at hand was insufficient for its examination, but the barium salt was prepared, and has the formula—

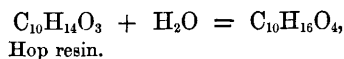


The resin (*a*), referred to above, which is separated during the evaporation of the alcoholic extract from the charcoal, has the composition $C_{10}H_{24}O_3$, and forms compounds with lead, barium, and calcium. The substance (*c*) is probably an oxidation product of the essential oil of hops, and is produced as follows:—

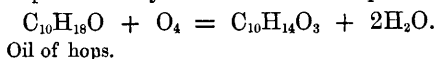


Such substances are often produced during the exhaustion of any plant with alcohol, being at first soluble, but after evaporation of the alcohol become insoluble. The results are then, that in the hop are contained a pseudoglucoside, $C_{29}H_{46}O_{10}$, which splits up into "lupulic"

acid and lupuliretin, which last is formed from the hop resin by taking up the elements of water—



and this resin is produced by an oxidation of hop oil—



whilst the substance (c) insoluble in ether, is produced by simple oxidation of the oil of hops, $\text{C}_{10}\text{H}_{18}\text{O} + 5\text{O} = \text{C}_{10}\text{H}_{18}\text{O}_6$. E. W. P.

Resin of Leptandra. By J. U. LLOYD (*Pharm. J. Trans.* [3], 11, 370—371).—The author is of opinion that the resin of leptandra of commerce does not consist merely of the resin precipitated by pouring an alcoholic extract of *Leptandra virginica* into water.

To prepare the resin, the root is extracted with alcohol, the extract is evaporated to the consistency of a syrup, and poured into ten times its volume of water, when the resin separates out. The supernatant liquid from this is decanted and boiled with 5 per cent. sulphuric acid until it loses its bitter taste, and a further quantity of resin is thus separated. The precipitated resin is heated in a steam-bath with constant stirring until it reaches such a consistency that when cold it will break; it is then broken into fine pieces and exposed to the air to dry. The resin precipitated by the sulphuric acid is dried by simply exposing it to the atmosphere. The solid alcoholic extract is prepared by mixing the extract evaporated to the consistency of a thick syrup with some of the dried resin prepared as above, and finally drying the mixture in a current of warm air.

The author considers that the bitter principle which remains in solution after the alcoholic extract is poured into water is a glucoside, but gives no proof of the fact other than the taste disappears when the solution is boiled with sulphuric acid. L. T. O'S.

Gloriosa Superba. By C. J. H. WARDEN (*Pharm. J. Trans.* [3], 11, 495—496).—With a view to throw light on the poisonous principle of the *Gloriosa superba* (an Indian plant, nat. ord. Liliaceæ) the author has undertaken a chemico-physiological research. The botanical characters of the plant are fully described. Its juice has a strongly acid reaction and slightly bitter taste; the old roots have a sweet taste.

The root of the plant collected before flowering, when cut and dried in the air, in some parts assumes a yellow colour, which is also produced by moistening the root with an alkaline solution; the colour is destroyed by acids. The fresh roots contain 81.06 per cent. moisture. The amount of extractive matter in fresh and old roots differs, that of the latter being much less than that of the former—

	New root.	Old root.
Alcoholic extract	13.01	6.05
Aqueous „	23.98	19.41
Ash.....	4.58	4.47
		i 2

The aqueous extract of the fresh roots is of a reddish colour, has a bitter taste and strongly acid reaction; it reduces Fehling's solution; contains a trace of tannic acid; caustic alkalis darken its colour.

The alcoholic extract contains a dark and light resin (α and β), also a bitter principle, *superbin*. These are separated by pouring the concentrated extract into water acidulated with acetic acid. The two resins are precipitated; the solution is neutralised with sodium carbonate and filtered from a trace of resin which is thrown down; the filtrate is acidulated with sulphuric acid and precipitated with tannic acid. The precipitate is collected, mixed with an equal bulk of lime and a little water, the mass dried, and extracted with boiling alcohol. On evaporating the alcoholic solution *superbin* is left: it is a violent poison, 0.047 gram being sufficient to kill a full-grown cat.

The resins are separated by treating the mixture with benzene, in which the β -resin is soluble and the α nearly insoluble. The trace of α -resin dissolved is separated by evaporating the solution until all the benzene is expelled, and agitating the residue with ether and sodium carbonate; the β -resin is dissolved and the α -resin remains in combination with the sodium carbonate; on evaporation, the β -resin is obtained.

The dark resin is purified by repeated solution in potash and precipitation by dilute acid. Another method to separate the resin is to treat the root with lime and digest with alcohol, when the β -resin is dissolved, or by dissolving the mixed resin, in alcohol, adding milk of lime, and after evaporating to dryness boiling out the β -resin with alcohol. The α -resin which remains apparently in combination with the lime may be separated from it by heating with dilute hydrochloric acid.

Tartaric acid is also contained in the root.

Gloriosa superba and *Scilla maritima* belong to the same family; it is probable that their active principles are closely allied, if not identical.

In a future paper, the chemical properties and physiological actions of the various constituents will be described.

L. T. O'S.

Viburnum Prunifolium. By H. ALLEN (*Pharm. J. Trans.* [3], 11, 413—414).—The alcoholic extract of the root of *Viburnum prunifolium* contains a colouring matter which is precipitated on addition of lead acetate, and a brownish resin of very bitter taste, which it is impossible to obtain free from sugar; it is, however, probably a glucoside. The colouring matter, from which the lead is separated by means of sulphuretted hydrogen, gives with gelatin a brown precipitate of tannate, with ferric chloride a greenish-black. It has an astringent slightly bitter taste. The lead sulphide precipitate, when boiled with alcohol, gives a solution yielding precipitates with mercuric chloride, ferric chloride, soda and potash, and with lead acetate.

The ethereal extract yields viburnin, obtained by Krämer from *Viburnum opulus*, a yellowish-green mass with bitter taste, soluble in alcohol, sparingly soluble in water. The residue from the ethereal

extract, when treated with water, yields oxalic, malic, and citric acids.

By extracting the bark with water and distilling the extract with sulphuric acid, valeric acid is obtained.

The ash, which amounts to about 9 per cent., consists of the sulphates and chlorides of calcium, magnesium, potassium, and iron.

L. T. O'S.

Eriodictyon Californicum. By W. C. HOLZHAUER (*Pharm. J. Trans.* [3], 11, 170).—The leaves were exhausted with alcohol and with water. The alcoholic extract contained a pale yellow volatile oil, lighter than water, of aromatic taste and smell; and a yellowish-white crystalline substance, tasteless and odourless, insoluble in cold water and benzene, sparingly soluble in hot water, imparting to it an acid reaction, very soluble in chloroform, ether, and alcohol. Tannin was also found in the extract.

In the aqueous extract gum was detected, associated with some brown colouring matter and with tannin.

On adding water to the ethereal extract, a resinous precipitate was obtained, and the supernatant liquid contained a crystalline substance similar to that contained in the alcoholic extract.

The resinous precipitate consisted of a vegetable wax, caoutchouc, and a brittle resin of amber colour, having an aromatic slightly bitter taste and a faint odour.

L. T. O'S.

Aralia Spinosa. By L. H. HOLDEN (*Pharm. J. Trans.* [3], 11, 210).—The barks of the *Aralia spinosa*, or false prickly ash, and the *Xanthoxylum*, or true prickly ash, differ very much in their physical properties.

The former presents a comparatively large number of spines, about a quarter of an inch long, thin, slender, tapering to a fine point, having round or oval bases; the bark breaks with tough, but nearly smooth fracture. The latter has only a few spines of the same length as those of the former but with two edged with linear bases of about three-quarters of an inch in length. The bark is brittle, and has a non-fibrous fracture.

The *Aralia spinosa* bark is extracted with alcohol, and the extract evaporated to dryness; the residue mixed with alcohol to form a paste is treated with benzene, which removes the fat. The residue is then exhausted with ether to remove tannin and resin. The tannin gives a precipitate with lead acetate, a green colour with ferric salts, and a ruby-red with potash. It coagulates albumin, is astringent, and soluble in ether, alcohol, and water. The residue is a brown opaque fusible solid, volatile at high temperatures; it is slightly acid; soluble in alcohol and ether, but insoluble in water, benzene, and chloroform.

When the residue from the alcoholic extract is dissolved in water and the solution treated with lead acetate, a precipitate is formed, which carries down mechanically the bitter principle; this may be separated by washing the precipitate with alcohol. On evaporating

the alcoholic solution, a light yellow glucoside is obtained, to which the name *araliin* is given. It is neutral, soluble in alcohol, dilute acetic acid, and water, with which it froths excessively on agitation; it is insoluble in benzene, chloroform, and ether. Hydrochloric and sulphuric acids bleach araliin, the characteristic odour of the plant being evolved. It gives no precipitate with lead acetate, platinum chloride, or mercuric chloride; it does not give any of the reactions for the alkaloids.

When araliin is dissolved in dilute hydrochloric acid and the solution is boiled, a white, tasteless, and odourless precipitate is formed, for which the name *araliretin* has been adopted. The solution contained sugar. When araliin is boiled with potash, an amber colour is produced. Tannic acid, on boiling, produces a flocculent precipitate.

L. T. O'S.

Analysis of Damiana. By A. B. PARSONS (*Pharm. J. Trans.* [3], **11**, 271—272).—The results of the analysis of *Damiana* (*Turnera aphrodisiaca*) are:—

Moisture, at 115—125° C.....	9·06
Ash.....	8·37
Chlorophyll, soft resin and volatile oil	8·06
Hard brown resin.....	6·39
Sugar, colour, and extractive matter.....	6·42
Tannin.....	3·46
Bitter substance.....	7·08
Gum.....	13·50
Starch isomerides.....	6·15
Acid and alkali extracts.....	10·02
Albuminoids.....	14·88
Cellulose.....	5·03
	<hr/>
	98·42

The medicinal properties of *Damiana* may be attributed to the presence of—

(1.) Volatile oil, which seems to be allied to the terebinthinate oils.

(2.) Soft resin, an oleo-resin in consistence, having a brown colour and very acrid taste, soluble in alcohol (80—90 per cent.), chloroform, ether, carbon bisulphide, benzene, and light petroleum; it is only sparingly soluble in ammonia and potash. It produces unpleasant irritant effects.

(3.) Hard brown resin (m. p. 85°) is tasteless, soluble in alcohol; forms soluble soaps with ammonia and potash. It probably consists of two different resins and some colouring matter.

(4.) Bitter principle of light brown colour. It is amorphous, soluble in water and alcohol, but insoluble in ether, chloroform, benzene, light petroleum, and carbon bisulphide. It is not a glucoside, nor does it yield a precipitate with lead acetate; it is a very valuable tonic.

(5.) The gum, which is contained in large quantities in the plant is white, but becomes black on exposure to the air.

(6.) The tannin has no astringent properties, but gives a greenish-brown colour with ferric salts. Damiana appears also to contain minute quantities of volatile and non-volatile organic acids, which give a purple precipitate with ferric chloride; these are not included in the above analysis.

L. T. O'S.

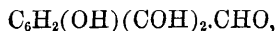
Coal. By H. REINSCH (*J. pr. Chem.* [2], **22**, 188—191).—The author's son, P. Reinsch (*Bot. Centr.*, **4** and **5**, 1880), from a microscopical examination of coal, finds that it consists for the most part of translucent globules, 0.13 to 0.24 mm. in diameter, giving a black cross with polarised light; besides which, there is a dark opaque fibrous structure of diverse form, and rarely occurring in cell-like formations. The properties of the globules reminded the author of those of chenopodin found by him in 1863 in *Chenopodium album* (*Neu. Jahrb. f. Pharm.*, **20**, 268).

In order to ascertain whether the globules consisted of chenopodin, some powdered coal was boiled with water, but the soluble product was found to be chiefly sodium chloride, with traces of iron and no chenopodin. By extracting the portion insoluble in water with alcohol (94 per cent.), a clear yellowish solution was obtained, blue by reflected light, and having an odour of coal-tar. This solution was concentrated by distillation on the water-bath. On cooling, a very small quantity of delicate snow-white flakes were found in the upper portion of the retort; these resembled chenopodin, and appeared under the polariscope as a net of delicate polarising needles. The residue in the retort had a slight smell of tar. On evaporating a drop, distinct crystals were obtained, showing no cross, however, under the polariscope. The distilled spirit was perfectly clear, but slightly fluorescent, and when mixed with a large quantity of water, became bright blue by reflected light. The author considers the crystalline body, which partly evaporates with the alcohol, to be altered chenopodin.

No crystalline sublimate was obtained by the dry distillation of coal at the temperature of melting lead. From the quantity of water obtained, the author considers that coal contains more than 5 to 8 per cent. of oxygen (numbers usually given for oxygen + nitrogen). In conclusion, the author directs attention to his observation of the large amount of phosphoric anhydride in coal (*Jahresb.*, **26**, 317), which in coals he examined amounted to 1 per cent., and this, on burning the coal, necessarily escapes into the air, since coal ash contains mere traces of phosphoric anhydride. The atmosphere is accordingly not only a source of carbonic anhydride for plants, but also, from the large amount of coal consumed, a source of phosphoric anhydride.

F. L. T.

Composition of Aesculin and Aesculetin. By C. LIEBERMANN and R. KNIETSCH (*Ber.*, **13**, 1590—1596).—According to the authors, *acetylaesculetin* contains only two acetyl groups, and has the formula $C_9H_4O_4\dot{A}c_2$, instead of three such groups, as stated by Nachbauer and Schiff. Hence Schiff's formula for aesculetin,



is doubtful. It only admits of the introduction of two bromine atoms into the benzene group or into the molecule of aesculetin, whilst Liebermann and Knietzsch obtained on heating a solution of the substance in glacial acetic acid with three molecules of bromine, a yellow crystalline powder, which after crystallisation from alcohol forms long yellow needles, $C_9H_3Br_3O_4$ (m. p. 240°). Tribromaesculetin treated with sodium acetate and acetic anhydride, yields *tribromdiacetaesculetin*, $C_9HBr_3(\bar{A}cO)_2O_2$, crystallising from alcohol in long, white, very thin needles (m. p. $180-182^\circ$). The same compound is formed by the action of bromine on a hot solution of acetaesculetin in glacial acetic acid.

The authors confirm Rochleder's empirical formulæ for aesculetin, $C_9H_6O_4$, and for aesculin, $C_{15}H_{16}O_9$.

Aesculin, recrystallised from its aqueous solution, loses 24 per cent. = $1\frac{1}{2}H_2O$ on drying at $120-130^\circ C$. If bromine is gradually added to a cooled solution of aesculin in glacial acetic acid, a white precipitate of dibromaesculin (m. p. $193-195^\circ$), $C_{15}H_{14}Br_2O_9$ is obtained. It yields needles of a *dibrompentacetaesculin*, $C_{15}H_9\bar{A}c_5Br_2O_9$ (m. p. $203-206^\circ$). Treated with concentrated sulphuric acid, it yields *dibromaesculetin*, $C_9H_4Br_2O_4$, slightly soluble in water, and crystallising from alcohol in yellowish needles (m. p. 233°), which may be converted into *dibromdiacetaesculetin*, $C_9H_2\bar{A}c_2Br_2O_4$ (m. p. 177°). O. H.

Aspidospermine and Paytine. By N. WULFSBERG (*Pharm. J. Trans.* [3], **11**, 269—271).—The author makes a botanical comparison between the "white payta bark," which yields paytine, and the "white quebracho bark," which yields aspidospermine, and then proceeds to make a comparison between the chemical results obtained by Hesse with paytine (*Annalen*, **154**, 287), and by Fraude with aspidospermine (*Ber.*, **11**, 2189, and **12**, 1560).

Paytine.

Colourless prisms.
Bitter taste.
Readily soluble in alcohol and ether.
Sparingly soluble in water.
M. p. $156^\circ C$.
Heated above m. p. chars, and yields oily distillate.
Crystalline hydrochloride, hydriodide and nitrate. Sulphate, oxalate, chromate, and nitropicrate are amorphous.
Hydrochloride soluble in 16.6 parts water at 15° .

Aspidospermine.

White prismatic crystals, with simple shining facets.
Bitter taste.
Soluble in 48 parts alcohol (99 per cent.) at $14^\circ C$, and in 136 parts ether at $14^\circ C$.
Sparingly soluble in water.
M. p. $205-206^\circ C$.
Heated above m. p. decomposes, evolving irritating vapour, having some resemblance to odour of acrolein.
Does not form crystalline salts.
Hydrochloride readily soluble in water.

Paytine.

Solutions of hydrochloride precipitated by mercuric chloride (yellowish).

Picric acid gives yellow flocks.

Chromate, a yellow amorphous precipitate.

Hydrochloride gives with PtCl_4 a yellow precipitate, which when boiled with hydrochloric acid, gives a brown-red solution, changing in colour to blue, with separation of blue precipitate.

Aspidospermine.

Mercuric chloride gives white precipitate with hydrochloride.

Picric acid yellow precipitate.

Potassium chromate and dichromate give yellow precipitates in concentrated solutions.

PtCl_4 gives yellow flocculent precipitate, which when dissolved and boiled with PtCl_4 is coloured deep violet.

From this comparison the author considers it probable that these two alkaloids are identical.

The different formulæ proposed for the two compounds by the two authors may be explained by the fact that Hesse dried his paytine at 130° — 140° C., whereby 1 molecule of water of crystallisation is driven off. And, moreover, he finds that in different samples crystallised from different solvents, the water of crystallisation behaves very differently; Fraude, however, states that in the preparation of aspidospermine, a high temperature is to be avoided. If, then, to Hesse's formula for paytine, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$, a molecule of water be added, a formula is obtained agreeing more closely with the result of Fraude's analyses than either of the formulæ proposed by him (viz., $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2^*$ and $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_2$). The results of the analyses of the platinochloride do not correspond very well on account of the reducing action of the alkaloid.

The geissospermine of Hesse is distinguished from aspidospermine and paytine by its sparing solubility in ether, and the purple-red colour it gives with nitric acid; it does not reduce platinum chloride, and has the formula $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

Should the identity of these two alkaloids be established, the author proposes to retain the name *paytine*. The payta-bark on account of its richness in starch and the absence of volatile compounds, is suitable for the manufacture of brandy.

L. T. O'S.

Ditaïne. By E. HARNACK (*Ber.*, 13, 1648). Controversial reply to Hesse (*Annalen*, 203, 144).

Lepidine. By S. HOOGEWERFF and W. A. VAN DORP (*Ber.*, 13, 1639—1640).—When cinchonine is decomposed by potash, lepidine is found in considerable quantity in that portion of the product which boils at 250° — 270° . It was obtained in a pure state by precipitating the solution of the acid sulphate with alcohol, recrystallising the sulphate, and decomposing it with potash. Lepidine prepared in this way

* The analytical results do not agree with this formula.

boils at 256—258°. Its *acid sulphate* $(C_{10}H_9N)_2H_2SO_4$, crystallises in needles; the *dichromate*, from hot water, in golden-yellow needles, which become brown when exposed to light, and decompose at 100—110°. *Lepidine platinumchloride* $(C_{10}H_9N.HCl)_2PtCl_4 + 2H_2O$, forms orange-red needles. With silver nitrate, lepidine yields white needles $(C_{10}H_9N)_2AgNO_3$, fusing below 100°.

On oxidation with alkaline permanganate, lepidine first yields *methyl pyridinedicarboxylic acid*, which is subsequently converted into *pyridinetricarboxylic acid*.

Lepidine therefore should be considered as a methylquinoline.

O. H.

Apophyllic Acid. By E. v. GERICHTEN (*Ber.*, **13**, 1635—1638). On treating apophyllic acid with hydrochloric acid (sp. gr. 1.185) at 240°, methyl chloride is produced, together with a nitrogenous acid. The latter crystallises in short prisms (m. p. 266—268°), and sublimes with partial decomposition; the solution is precipitated by lead, silver, and barium salts. Copper acetate produces no change in the cold, but on heating a flocculent precipitate separates, which redissolves on cooling; on prolonged heating, it becomes crystalline, and then remains insoluble in cold water. Ferrous sulphate does not produce a precipitate. When the acid is heated with soda-lime, it decomposes with formation of *pyridine*. Its composition is represented by the formula $C_7H_5NO_4$, and corresponds with that of a *pyridinedicarboxylic acid*, $C_5H_3N(COOH)_2$. It appears to be identical with that obtained by Hoogewerff and van Dorp (*Ber.*, **13**, 61), and with the *cinchomeric acid* of Weidel (*Ber.*, **12**, 1145).

The author is of opinion that the cinchona alkaloids and those of opium must also be considered to be derivatives of pyridine and quinoline.

Cotarnine appears to contain the COOMe group of apophyllic acid.

O. H.

Investigation of the Processes of Decomposition occurring during the Rotting of Eggs. By C. O. CECHE (*J. pr. Chem.* [2], **22**, 338—344).—The main causes of rotting are high temperature and moisture. The various stages of decomposition are classed in seven groups:—(1.) When exposed to warmth and moisture and not fertilised, the albumin first becomes watery, and the membrane inclosing the yolk bursts, allowing a partial mingling to occur at the surface of the contact of the yolk and albumin. (2.) As the decomposition proceeds the contents become a homogeneous cheesy mass, first white, then yellow, and finally greenish in colour. (3.) They then gradually change into a yellow or greenish liquid. (4.) If the fresh unfertilised egg is kept at rest and at a constant temperature of about 14° with exclusion of moisture, the yolk remains entire, and after the gaseous products of decomposition and the water of the albumin have escaped by diffusion through the shell, the residue forms a crust round the flattened yolk, the shell appearing half empty. (5.) When the outer part of the yolk is very firm, the decomposition is often limited to the albumin, the yolk remaining unaltered in form as a black mass. (6.) In fertilised eggs, containing the “tread,” the decomposition

commences at the middle of the egg, and the albumin is often unaltered whilst the yolk has become watery. (7.) All the above-mentioned changes proceed with a rapidity dependent on the temperature and moisture of the air, and on whether the eggs are at rest or not. Sometimes the pores of the shell become closed, and the gaseous products become confined under pressure, causing the egg to burst spontaneously or when opened.

The author reserves the account of qualitative and quantitative changes occurring during these seven kinds and stages of putrefaction for another paper, and considers only the possibility of applying rotten eggs to some technical purpose.

A number of rotten eggs were freed from their shells, and the contents evaporated to dryness, partly in mass and partly in groups as above. A fatty mass, free from the smell of rotten eggs, was obtained; and from this an amount of oil was extracted which equalled in amount that obtainable from an equal quantity of fresh eggs. The residue was a dirty white earthy mass containing coagulated albumin, nitrogenous substances and salts. Studied in groups, it was found that eggs from class (3) contained from 2 to 3 per cent. less oil than fresh eggs; but eggs from class (2) gave an excess of from 1 to 2 per cent., and from class (4) all the oil of the fresh egg was obtainable. Rotten eggs on an average yielded 10.5 per cent. of oil, whilst from fresh eggs 11.27 per cent. was obtained.

The entire dried residues, as well as the extracted oil, could be easily saponified with soda; the soap thus obtained is perfectly free from smell, and forms a good lather; the dry particles in the residue which remain unsaponified, impart to the soap a mottled appearance, and in no way spoil its smell or appearance. If the fat is extracted before being saponified, the residue would be valuable for the preparation of manure, since the ash of the yolk contains 60.1 per cent. of phosphoric acid.

F. C.

Researches on the Physical Chemistry of Blood. By G. HÜFNER (*J. pr. Chem.* [2], 22, 362—388).—The author minutely describes investigations undertaken with freshly devised apparatus, the object of which was to redetermine the number of c.c. of oxygen at 0° and under 1 metre pressure, which 1 gram of the colouring matter of the blood can retain in feeble chemical combination. The result thus obtained leads also to a revision of the molecular weights of hæmoglobin and oxyhæmoglobin.

The absorption coefficient, as above defined, had been already found to be 1.16, after the experimental result had been corrected for the oxygen absorbed by the serum, assuming that liquid to have the same coefficient of absorption as water. This assumption being unproved, and the correct determination of the coefficient being necessary for the spectrophotometric determination of oxygen in blood, the further examination was undertaken.

The fundamental expression, $k = ah + bp$, where k = the total volume of gas absorbed reduced to 0° and 1 metre pressure, h = the quantity of hæmoglobin present, p = the pressure under which absorption occurs, a is a constant representing the quantity of gas chemically

held by unit of colouring matter, b the quantity absorbed by the liquid, and varying with the pressure p . The constants were determined from a large series of experiments, in which h and k were noted when the temperature was uniform, but pressure varied. In the first set of absorptiometric experiments, carbonic oxide was used instead of oxygen, because it is free from the source of error arising from the combination of oxygen with the metallic impurities of the mercury and the organic matters present in the blood.

Preparation of Reduced Blood Solution.—Defibrinated dog's blood was diluted from eight to ten times, and reduced by passing through it hydrogen gas prepared from zinc and dilute sulphuric acid, and purified by passing through potassium permanganate solution, soda solution, and water successively. A special apparatus was used to prevent loss of the blood by frothing. After about two hours, 200 c.c. changed to a beautiful purple-violet colour, and showed only the reduction-band in the spectrum. The liquid was then transferred to a bulb provided with two stopcocks, and exposed to a Sprengel vacuum at a temperature of 30° to remove all hydrogen and carbonic anhydride from solution. It was then preserved in the bulb, the stopcock of which had been closed after the vacuous portion had been allowed to fill with mercury.

Determination of the Hæmoglobin.—The quantity of hæmoglobin was estimated as oxyhæmoglobin by the spectroscope in the way already described (this Journal, 16, 310), and after dilution to an extent estimated by careful weighing, the determination was always made in liquids of two different degrees of dilution, and also for each liquid on two different regions of the spectrum. The accuracy of the determination, as well as the purity and suitability of the liquid, was thus made certain.

The absorptiometer employed by the author was a modified form of Wiedemann's; it is figured and fully described. Its principle consists in agitating the known volume of reduced blood solution with an excess of the pure gas in a vessel closed by stopcocks, and then ascertaining the weight of mercury which enters after agitation owing to the absorption of a portion of the gas, precautions being taken to prevent the contact of the blood and gas whilst the latter is being introduced, and to maintain the temperature and pressure of the gas uniform both before and after agitation. The mercury to be weighed was obtained after the agitation in a pulverised condition, and required treatment with strong sulphuric acid to cause the minute globules to unite; it was then washed and dried. The gas was always employed in a moist condition. In all cases experiments were made with two such apparatus, capable of holding different quantities of blood. The trustworthiness of this apparatus was first proved by determining by its means the coefficient of absorption of carbonic anhydride; the number obtained closely agreed with that found by Bunsen. Since the blood solution could not be long preserved unaltered, it was necessary to make a number of sets of determinations, each set requiring a freshly made solution.

From a number of experiments with carbonic oxide, the value of $a = 1.20$, and of $b = 0.6305$; the latter divided by the volume of blood

solution gives 0.01979, a coefficient for serum less than that for pure water.

Experiments were then made with oxygen: the results obtained with this gas showed much more variation than those with carbonic oxide. The constants found were as follows: $a = 1.25$; $b = 2.117$. From the latter, it appears that the coefficient for serum is greater than that for pure water, a result doubtless due to the union of oxygen with the impurities of the mercury and the organic matter of the serum. Further experiments were made with pure aqueous solution of the colouring matter, to eliminate the latter source of error. In some experiments the coefficient for oxygen was found to be smaller than that for carbonic oxide. This was doubtless due to the evolution of carbonic anhydride formed by the oxidation of organic matter in the blood. Taking into consideration the probable error in each experiment, and calculating the coefficient (a) from the results obtained with both carbonic oxide and oxygen, the value 1.202 was obtained.

Two determinations were then made by allowing carbonic oxide to act on blood saturated with oxygen. The oxygen was thus replaced by carbonic oxide, and was determined by an analysis of the residual mixture of carbonic oxide and oxygen, which was removed by the Sprengel pump (*Zeits. f. Phys. Chem.*, **1**, 313). The author does not consider that this method gives the whole amount of oxygen, since some is fixed by union with metallic impurities of the mercury, by organic matter in the blood, and by the grease on the stopcocks. The numbers obtained in two experiments were 1.17 and 1.18.

Finally, *undiluted* defibrinated blood, which had been violently shaken with air at 20° and 727 mm. pressure, was freed from oxygen by the Sprengel pump, and the volume of oxygen was determined. After allowing for that dissolved by the serum, and determining the hæmoglobin by the spectroscope in a portion diluted 151 times, the coefficient of absorption was found to be 1.1988.

From all the above determinations, the most probable value of the coefficient appears to be 1.202.

Assuming that 1 molecule of hæmoglobin unites with 1 molecule of oxygen, the molecular weight of hæmoglobin would be 14,133, and of oxyhæmoglobin, 14,165: the numbers calculated from the most trustworthy results of analyses of oxyhæmoglobin are 14,129 and 14,161. These agree well with the formula $C_{336}H_{1025}N_{164}FeS_3O_{189}$ for hæmoglobin, and this would give for the coefficient of absorption for oxygen by calculation the number 1.202, which is identical with that found by the above experiments. Should this molecular weight be correct, it proves the molecule of hæmoglobin to be at least five times as heavy as that of albumin.

The author in conclusion expresses a hope that the determination of these constants may render possible the application of the simple and exact spectrophotometric method to the determination of the proportion of oxygen in the blood as it enters and leaves different organs at rest and repose, and thus lead to a knowledge of the "physiology of oxygen."

F. C.

Physiological Chemistry.

Nutritive Value of Glycerol. By E. MUNK and others (*Bied. Centr.*, 1880, 654—657).—Experiments with dogs showed that glycerol does not economise the decomposition of albumin in the organism, nor does it take the place of carbohydrates or fats when given as food.
J. K. C.

Relations between Work and the Decomposition of Food in the Body. By O. KELLNER (*Bied. Centr.*, 1880, 584—594).—In these experiments a horse was caused to go through the same amount of work every day, until the separation of nitrogen in the urine became constant. The work was then trebled, the diet remaining the same, and it was found that the quantity of nitrogen in the urine increased. This also occurred when larger quantities of nitrogenous food were given; and the amount of secreted nitrogen returned to the original limit only when a sufficient diet of farinaceous food was allowed, thus showing that the carbohydrates may be considered as a source of muscular activity. When an animal is in good working condition, about half the quantity of additional farinaceous diet may be expended in work.
J. K. C.

Hydrolytic Action of the Pancreas and Small Intestine. By H. T. BROWN and J. HERON (*Annalen*, 204, 228—251).—An aqueous extract of the pancreas, as well as the finely-divided gland itself, converts starch into maltose and achroo-dextrin (ξ). On prolonged standing, dextrose is also formed. Neither the aqueous extract nor the gland itself has any action on cane-sugar. The inversion of cane-sugar, noticed by some observers, is due to the development of bacteria. The small intestine has the power of inverting cane-sugar, of converting maltose into dextrose, and of acting on starch as a weak ferment. The tissue of the intestine is much more active than the aqueous extract. The action of the intestine seems to have no relation to the number of Lieberkühn and Brunner's glands, but to depend more on the distribution of Peyer's glands. In the conversion of starch into readily diffusible dextrose capable of assimilation, the action of the pancreas and Peyer's glands seems to be mutual and interdependent. The pancreas converts the starch into maltose, and the Peyer's glands then complete the process of conversion into dextrose.
G. T. A.

Phenol in the Animal Economy. By R. ENGEL (*Ann. Chim. Phys.* [5], 20, 230—240).—Wöhler was the first to show that benzoic acid during its passage through the animal system was converted into hippuric acid; and more recently Baumann has observed that phenol under similar circumstances is capable of combining with sulphuric acid, forming an ethereal sulphate, which is afterwards eliminated by the urine as a potassium or sodium salt; at the present day the existence of phenol in the urine, especially of herbivora, is well established. Again, Nencki has shown that indole and indican can be detected in the animal economy; the former is the result of the putre-

faction of albuminoïds, whether by decomposition in air, or by the agency of the pancreatic digestion, whilst a subcutaneous injection of indole is found to pass out of the system as indican; researches of the same nature have also established that phenol and other analogous compounds are produced by the putrefaction of albuminoïds together with indole, and that the quantity of indole diminishes exactly in proportion as the phenol increases; a portion of this phenol is eliminated in the excreta, but by far the greater part passes away in the form of potassium-phenyl sulphate as before stated.

Phenol appears also to be formed from another source. One of the most constant products of the decomposition of albuminoïds is tyrosine, a body which is found both in the spleen and pancreas, and which in certain cases of degeneration of the liver appears in notable quantity in the urine. The injection of tyrosine determines an augmentation of potassium-phenyl sulphate in the urine; there can be little doubt, therefore, but that the phenol is produced by the decomposition of the tyrosine.

To detect the presence of phenol, the liquid is acidulated with sulphuric acid and distilled, the distillate is tested either with iron perchloride which gives a blue colour, or with bromine-water; this latter reagent is exceedingly sensitive, giving even with very dilute solutions of phenol a white crystalline insoluble precipitate of tribromophenol. This reaction may also be made a quantitative one if required, the weight of the phenol present being equal to $\frac{28.4}{100}$ of the

weight of the tribromo-compound found. Baumann estimates the phenyl sulphate present in urine by precipitating and removing the sulphates with barium chloride and acetic acid, and then boiling the solution with hydrochloric acid; the ethereal sulphate is thus decomposed, and a fresh precipitate of barium sulphate is obtained. From the weight of the latter, the weight of phenyl sulphate present is easily calculated.

J. W.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation in the Roots of an Apple Tree. By P. v. TIEGHEM (*Bied. Centr.*, 1880, 688—689).—Owing, according to the author, to the great dampness of the soil, the cells in the roots of an apple tree underwent an alcoholic fermentation for some time, during which the tree presented a sickly appearance. J. K. C.

Fermenting Power of Diastase. By M. J. KJELDAHL (*Bied. Centr.*, 1880, 689—691).—The relation of the strength in diastase of two solutions of malt-extract may be expressed by their relative power of affecting a given weight of gelatinised starch under the same conditions, when the quantities of extract used are not very large: the limits of temperature between which the greatest fermenting action takes place are from 54° to 63°; the presence of small quantities of mineral acids assists the action. J. K. C.

Ammonia in Plants. By H. PELLET (*Bied. Centr.*, 1880, 673—675).—As the ammonia in beetroot seems to be present in the form of ammonium-magnesium phosphate, the finely-grated roots were digested with hydrochloric acid, and distilled with magnesia; 0.19 per cent. of ammonia was found in the dry root; part of this amount may, however, arise from the decomposition of amido-compounds present in the plant. Similar experiments were made with the liquid expressed from muscle, and with yeast. Ox muscle gave 0.15, and yeast 0.059 per cent. ammonia.

J. K. C.

Chemical Composition of Linseed. By A. LADUREAU (*Bied. Centr.*, 1880, 670—671).—Russian linseed when grown in France becomes valueless after the second generation: according to the author, this is due to the ash of the seed losing more than half its phosphoric acid by being cultivated in French soil.

J. K. C.

Composition of Oats. By L. GRANDEAU and A. LECLERC (*Bied. Centr.*, 1880, 669—670).—The authors have performed 120 analyses of oats; the mean result of these, together with the maximum and minimum quantity of each constituent, are given in the following table:—

	Mean.	Maximum.	Minimum.
Water	12.01	15.50	8.50
Protein	9.80	12.43	7.12
Nitrogen-free extract ..	59.09	64.65	48.60
Fat	4.58	7.13	2.77
Fibre	11.20	14.89	6.73
Ash	3.32	6.14	2.06

J. K. C.

Fattening of Oxen. By A. VOELCKER (*Bied. Centr.*, 1880, 660—661).—A comparison of the fattening effects of oil cake with that of a mixture of Indian corn meal and cotton seed cake, given as fodder to young oxen, was in favour of the latter mixture, both on the score of cheapness and efficiency.

J. K. C.

Cultivation of Furze. By SCHIRMER-NEUHANS (*Bied. Centr.*, 1880, 678—679).—On dry soils, the cultivation of dwarf furze as fodder may be substituted with advantage for clover: analysis of the dried substance gave the following results:—Ash, 5.78; fibre, 46.80; albumin, 9.76; fat, 1.92; nitrogen-free extract, 35.74 per cent.

J. K. C.

Use of Lupines as Fodder. By v. PUTTKAMMER and others (*Bied. Centr.*, 1880, 661—664).—The favourable effect of steaming on lupine seeds has been confirmed in many cases by the authors.

J. K. C.

Cultivation of Soja Bean. By C. O. HARZ (*Bied. Centr.*, 1880, 671—673).—Various kinds of this bean were planted in the neighbourhood of Munich, but did not thrive in a satisfactory manner, as the climate was too cold for them.

J. K. C.

Cultivation of various kinds of Beet. By J. GODEFROY and A. DOUDOUY (*Bied. Centr.*, 1880, 652—654).—Chemical manures such as sulphate of ammonia, superphosphate, &c., gave better results with the larger kinds of roots than stable dung: the “mammoth” produced the largest crop.
J. K. C.

Drainage Water from Moorland. By R. SCHILLER (*Bied. Centr.*, 1880, 636—638).—The water contained generally about 100 grams of dissolved solids to the gallon, consisting chiefly of sulphates of lime and magnesia: the amount of nitrates was greater in the summer months than in winter.
J. K. C.

Behaviour of Phosphates in Water charged with Carbonic Acid. By H. ALBERT and R. WAGNER (*Bied. Centr.*, 1880, 640—647).—The authors find that precipitated dicalcium phosphate is easily soluble in water charged with carbonic acid, and is not thrown down by calcium carbonate: solutions of alkaline nitrate or carbonate also readily dissolve this phosphate. Precipitated phosphate of iron or alumina is not so easily attacked by any of these solvents, especially if it has been well dried. All kinds of soil absorb phosphoric acid from these solutions, the amount of absorption being determined by the time of contact only in the case of soils rich in lime, and in this respect carbonic acid solutions of dicalcium phosphate play the same part as aqueous solutions of superphosphate, the absorption being the more complete the more lime there is present in the soil.
J. K. C.

Organic Matters in Soil; Examination of Grandeau's Theory. By O. PITSCH (*Landw. Versuchs.-Stat.*, 26, 150).—This long paper is a report of the author's examination of the theory of Grandeau as to the value of humus in the soil.

The words employed by Grandeau himself when enunciating his theory in the “*Annales de la Station agronomique de l'Est*” are as follows:—

1. The mineral constituents of the soil are the true nourishment of plants, and have the property of traversing vegetable tissues, the roots inclusive. 2. Organic matters are of the highest importance in the development of vegetables. They are not themselves assimilated by the roots, but play the part of media between the soil and the plant; they combine with mineral matters, and form soluble compounds, which the roots of the plants decompose in their turn, seizing on the inorganic and leaving the combustible matter untouched. This matter is the indispensable vehicle required to transfer and render available the mineral matters powerless to nourish plants without their help. 3. Fertile soils offer their mineral ingredients to plants in a state similar to that in which they are contained in stable manures.

This theory, if correct, would give a new insight into the nourishment of plants, and as Grandeau estimates the valuable combinations of humus with inorganic substances by the amount of so-called “*matiere noire*,” which can be extracted from the soil by ammonia, it would then offer an easy method of calculating the value of all soils,

and not only so, but would enable the farmer to bring his soil up to any desired standard of fertility. The opinions of practical men agree to a certain extent with this theory (Ville and his followers excepted), and it has found considerable confirmation from the experimental cultivation of sandy soils—in certain instances the mixture of peaty soil with sand and road-scrappings giving exceedingly good results. The author asserts that all or nearly all Grandeau's own experiments were made with sandy and forest soils, that few or none were made with true clays, and that the physical condition of the soils so experimented on, caused by the addition of the organic matter would in great part account for the successful results. Impressed by the importance of the subject, the author undertook its searching examination. He obtained samples of 13 soils from various farms in the Netherlands, the cultivators of which gave him full information as to their methods of farming, and the productiveness of their soils. The method employed by Grandeau for the separation of his "matiere noire" was to place 300 or 400 grams of the clay in a large funnel, in which was a smaller one containing pieces of broken glass or porcelain, remove the lime by treatment with dilute HCl (10—25 c.c. to the litre of water), wash the residue to neutral reaction and dry. An aliquot part was then exhausted of its "matière noire" by dilute ammonia (half water), the filtrate evaporated to dryness, ignited, and the P_2O_5 estimated in the ash; the author suggests certain improvements, but they are unsuitable for abstraction.

Even with modifications, however, the author does not think that this mode of soil examination will displace that already in use; he allows that it may prove a valuable addition to present methods, and thinks, as a result of the many analyses performed during the investigation, that the amount of P_2O_5 contained in the ammoniacal extract is even a better measure of the productive capacity of different soils than is the quantity of P_2O_5 found in the acid extract as now prepared.

An improvement, he believes, would be to estimate the P_2O_5 in both ways; then should the acid extract contain a large, and the ammoniacal a small percentage, the soil would require a manure rich in organic matters; if the reverse be the case then one containing abundance of phosphates should be applied, whilst if both extracts are proportionally poor or rich the fertility of the soil will be less or greater accordingly.

These conclusions, however, are considered as independent of the theory of plant nutrition under examination, which requires that although plants can by their roots extract nutritious matter, not only from solutions, but from the solid particles with which they come in direct contact, still profitable results cannot be obtained unless solvents be present to offer a ready supply to their roots. And further that it is the presence of humus matter which causes the transfer of the inorganic matter to the plant by directly modifying the chemical character of these mineral combinations. The author does not agree with this view, and thinks it more reasonable to believe that the roots of the plants or matters in the soil other than humus have a solvent power similar to that of acids.

He reviews some of the experiments relied on by Grandeau as proof of the correctness of his views, one being the growing of certain seeds in quartz sand, exhausted with acid, washed, and supplied with dilute "matiere noire;" the experiment proves simply that it is *capable* of nourishing plants, but proves nothing more, and from elementary analyses of two samples of that substance, the author found it to contain all inorganic substances required for the nurture of vegetables; that it does yield those matters is not denied, but for the support of the theory it must be further proved that the presence of humus is *indispensable*, and sufficient evidence of this had not been adduced. Another experiment of Grandeau referred to, is one in which a sample of Russian black earth was divided into two portions, one exhausted of its "matière noire," the other not; kidney beans were planted in both, in the exhausted sample the show of leaves was extremely small, and they quickly shed, in the other portion the growth was healthy and development of leaves normal. The author's explanation of this is that the treatment with dilute ammonia necessary to remove the "matiere noire" removed at the same time the inorganic nutritive matters formerly present.

Another experiment relied on by Grandeau is one in which four boxes, each a square meter of surface, were planted with various seeds, two boxes containing clayey and two light calcareous soil: one box of each was mixed with a certain proportion of peaty earth containing little phosphoric anhydride; the product of the boxes containing the admixture was in all instances considerably higher than the unmixed samples. Grandeau himself admits that the physical condition of the former was much superior to that of the latter; and in this fact our author finds sufficient explanation of increased production, it being allowed by all practical farmers that the diligent working of the soil considerably influences the crop. The author concludes that a critical examination of the proofs advanced shows that not one of them necessarily compels the adoption of the theory, whilst none of them are contradictory to it nor to other theories, previously either partially or wholly formulated by Simon, Mulder, and Dettmer.

Previous experiments of the author on the solubility of phosphates in ammonium citrate led him to try the effect of ammonium humate in the expectation that its behaviour towards phosphates would be similar; the process of obtaining the pure humic acid is described at length, and its combination with ammonia, but it is too long for abstraction. The ammonium humate was found in fact to exercise quite as solvent an effect on the phosphates as the ammonium citrate; and when mixed intimately in the soil during cultivation, it would come into so many points of contact with the particles of phosphate that it should exercise even a more potent effect.

The author concludes by declining to accept the theory of Grandeau, but admits the very great importance chemically and physically of humus in soils; he asserts, however, that its value varies with the *nature* of the soil; and, further, that whilst Ville and his followers who insist that inorganic substances are the only valuable manure materials err in one direction, Grandeau errs as greatly in the other by the exorbitant value he places on organic matter.

J. F.

Solubility of Certain Manure Materials. By A. MORGEN (*Landw. Versuchs.-Stat.*, 26, 51—75).—The number of nitrogenous substances employed in the manufacture of artificial manures is very large. An impression prevails that they all require about the same period of time for their decomposition in the soil, and chemical analysis attaches equal importance to the nitrogen contained in all. Practice, however, shows that the actual value of such substances to the farmer depends greatly on the time they require to decompose and render their valuable constituents available for plant nutrition.

The subject has not hitherto been experimentally treated in Germany, and the author of the present paper gives a report of numerous experiments intended to throw light on it. They were made with horn meal and leather meal, substances prepared from manufacturers' waste by steaming and drying. The experiments were divided into three series, in one of which the samples were treated with water for a lengthened period in the water-bath at a high temperature, with the addition in certain cases of a little sewage water to hasten decomposition. The second series was similar to the first, except that the samples were left exposed to the air at the natural temperature of the atmosphere in a garden. The third differed from the other two in treating, not equal quantities of the substances, but quantities containing equal amounts of nitrogen.

In the first series, 5 to 10 grams of each substance were placed in a litre of distilled water, with, in two cases, 5 c.c. of sewage water added, and kept at 30° C. in a water-bath for 131 days. The amount of nitrogen which had passed into solution at the end of that time was in the case of the leather meal one-third, and of the horn meal two-thirds of the total contained in the samples. The addition of sewage water does not appear to have affected the result, except in augmenting the amount of nitrogen in the form of ammonium compounds; the concentration of the solutions does not appear to have at all affected the results.

In the second series some of the specimens were boiled before submitting them to prolonged action of the air and sun. These showed slightly lower numbers, owing probably to the boiling having rendered albuminous substances insoluble. The total results were very similar to those of the first series, and strongly in favour of the horn meal.

The third series yielded slightly different yet generally similar results, and all the experiments confirm the verdict of practical men that the nitrogen in horn (and bone) meals is much more valuable as a manure ingredient than that contained in leather meal. It must be borne in mind that the whole object of the leather manufacturer is to render his leather insoluble, and that some mode of removing the tannic acid must be found before waste leather will be as easy of decomposition as bone or horn meal. J. F.

Experiments with Various Phosphates as Manure. By E. WEIN (*Bied. Centr.*, 1880, 647—651).—The soil in which these experiments were carried out was a mixture of sand and calcium carbonate. Peas and oats were manured in different plots with various forms of phosphate, soluble and insoluble, and in every case dicalcium phos-

phate yielded the best result. The author explains this by assuming that in the presence of excess of calcium carbonate, soluble phosphate of lime is converted into tricalcium phosphate, which is not readily absorbed by the roots, whereas dicalcium phosphate does not undergo this change.

J. K. C.

Pigeons' Dung. By E. WEIN (*Bied. Centr.*, 1880, 693).—A sample taken from a church tower gave the following results on analysis:—Water, 10·99; organic and volatile bodies, 56·65; ash, 33·36; nitrogen, 2·25; phosphoric acid, 2·04; and potash, 5·49 per cent.

J. K. C.

Manure for Fruit Trees. (*Bied. Centr.*, 1880, 693).—Experiments which were carried on in Potsdam showed the most suitable manure for fruit trees to be a mixture of potash sulphate and superphosphate, which increased the number of blossoms considerably.

J. K. C.

Manuring of Vines. By P. WAGNER and H. PRINZ (*Bied. Centr.*, 1880, 638—640).—Vines extract yearly from the soil only about three-fourths of the quantity of potash and phosphoric acid extracted by cereals; the amount of manure applied is, however, generally greater.

J. K. C.

Analytical Chemistry.

On Accurate Perception of Colour-change in Titration.

By A. DUPRE (*Analyst* [1880], 5, 123).—The author views the coloured liquid to be titrated through a glass cell filled with a solution of the same colouring substance as that contained in the liquid itself, and yielding a colour of about equal intensity. The change of tint becomes then strikingly manifest even in very dilute solutions.

The method has been tried in the titration of chlorides in drinking-water by standard silver nitrate, using neutral potassium chromate as indicator, a glass cell with parallel faces at little less than half an inch apart being filled with the neutral chromate solution, and interposed between the eye and the water contained in a porcelain dish.

The change of turmeric from yellow to brown is also readily perceived through a turmeric cell.

In titrating lime in water with decinormal sulphuric acid, the dish was half covered with a porcelain plate, and neutral cochineal solution was filled into the cell. At first the tint of the water is widely different from that of the porcelain plate, but when neutrality is reached these tints appear identical if the strength of the cochineal solution in the cell and in the water have been fairly matched.

The method will be generally applicable to all similar cases when a colour-change has to be accurately noted.

F. C.

Action of Uranyl Salts on Turmeric Paper. By C. ZIMMERMANN (*Annalen*, **204**, 224—225).—Uranyl salts colour turmeric paper brown. The nitrate has a much stronger action than the sulphate and acetate. The brown tint lies midway between that produced by alkalis and by boric acid. It may be distinguished from the first by its appearing in a faintly acid solution, from the latter by its disappearance on addition of free mineral acids.

The brown colour passes into a violet-black when sprinkled with diluted sodium carbonate, and this last is converted by hydrochloric acid into the original yellow, whilst the brown produced by boric acid is converted into a blue to black by sodium carbonate, and is restored on addition of hydrochloric acid. G. T. A.

Separation of the Heavy Metals of the Ammonium Sulphide Group. By C. ZIMMERMANN (*Annalen*, **204**, 226—227).—This is an appendix to a paper in the *Annalen*, **199**, 1, describing the separation of zinc from the other metals of the same group by means of ammonium thiocyanate and sulphuretted hydrogen. The most excellent results have been obtained by substituting thiocyanic acid, prepared as follows:—Two parts of lead acetate are shaken up with one part of ammonium thiocyanate; the precipitate is washed with cold water and decomposed by sulphuretted hydrogen. The sulphuretted hydrogen is then removed by a current of air.

The method of analysis is either to mix the liquid containing the metals with excess of sodium carbonate, or to neutralise it as nearly as possible. In the first case the precipitate is dissolved in the thiocyanic acid; in the second case some ammonium thiocyanate is added to the acid. The solution is then, if necessary, diluted, and sulphuretted hydrogen is passed into it. It is next warmed gently on the water-bath, and proceeded with according to the method described in the previous paper. G. T. A.

Occurrence and Estimation of some Nitrates in Vegetable Substances. By I. BING (*J. pr. Chem.* [2], **22**, 348—351).—Nitrates have been discovered and estimated in tobacco-leaves, and in various roots, leaves, and blossoms by Schlösing and others. The author has determined the nitrates in several kinds of Chinese tea, in mate, valonia, and coffee by Tiemann's modification of Schulze's process. The extract from about 20 grams of substance was concentrated, and mixed whilst nearly boiling with lead acetate in the smallest possible excess; the yellowish flocculent precipitate is washed by decantation, and finally filtered by suction. The filtrate, mixed with a little strong sodium sulphate solution, is evaporated down to about 20 c.c. and filtered from lead sulphate; it is then distilled with addition of a little paraffin to prevent frothing. The nitric acid is probably present in the form of potassium nitrate; calculated as such, the percentages found in the air-dried substances were as follows:—Four varieties of Chinese tea gave an average of 0.051; maté, 0.052; valonia, 0.075; and coffee, when raw, 0.054, when roasted, 0.041. It is evident, therefore, that a certain proportion of nitrates are destroyed during the roasting of coffee. An analysis of the maté showed that it closely resembled

Chinese tea in composition. The nitric acid was absorbed in every estimation by ferrous chloride, and there never remained more than 0.3 c.c. of unabsorbed gas. F. C.

Arsenious Sulphide as a Poison, and its Importance in Judicial Cases. By J. OSSIKOVSKY (*J. pr. Chem.* [2], 22, 323—338).—It is generally supposed that arsenious sulphide, whether chemically precipitated or in the form of auripigment, has no poisonous action on the living organism. A case of poisoning having occurred in which food containing arsenious sulphide was suspected, the author considers that arsenious oxide must have been present either as an original impurity or as a product by chemical change of the sulphide. A sample of auripigment was found by Tardieu to contain as an impurity much arsenious oxide, and the author considers it *à priori* possible that during the process of putrefaction of organic bodies arsenious sulphide may be converted into oxide by the action of ozone.

Experiments were made by exposing a mixture of arsenious sulphide, water, and pieces of decomposing pancreas to a temperature of 35—40° for a period of seven days; samples for analysis were removed at intervals and filtered, the filtrate on being acidified yielded a precipitate of arsenious sulphide, and the acid filtrate was tested for arsenious and arsenic acids. It was found that precipitated arsenious sulphide was much more rapidly oxidised under these circumstances than the more compact crystalline auripigment, but the result obtained from both forms of sulphide was similar. The albuminoid bodies present, on decomposition, yielded ammonia, which dissolved a portion of the sulphide as such; this was precipitated on acidifying the liquid with hydrochloric acid; the arsenious sulphide was also oxidised to arsenious acid, and to a smaller extent to arsenic acid; the quantities of these oxidation products formed increasing in proportion to the time. A considerable quantity of phosphoric acid was simultaneously formed from the pancreas.

Further experiments proved that in the absence of the pancreas, the presence of water at a moderate heat was sufficient to convert the precipitated arsenious sulphide into arsenious but not into arsenic acid.

The author further tried the effect of making the liquid, in which arsenious sulphide and decomposing organic matter were present, alkaline with sodium carbonate, so as to imitate the conditions existing in the large intestine where alkaline secretions would mingle with the food. It was found that the quantity of oxidised arsenic compounds formed was quite sufficient to produce poisoning.

The conclusions arrived at are:—

1. That during the decomposition of organic bodies easily oxidisable bodies are oxidised, and that arsenious sulphide under such circumstances is converted into arsenious acid, and to a small extent into arsenic acid. The precipitated sulphide undergoes oxidation more readily than auripigment.

2. In cases of poisoning by arsenious sulphide, the oxidation products appear more or less quickly, according to the nature of the decomposing body; the presence of water and heat also exerts much influence.

3. The quantity of oxidation products is directly proportional to the duration of the decomposition; hence it becomes impossible to determine whether sufficient arsenious acid was present to prove fatal at the time the food was taken when the suspected article has been submitted to examination only after a considerable interval. From a long-delayed chemical examination therefore conclusions cannot with certainty be drawn.

F. C.

Ash of Light-coloured Cod Liver Oil. By E. A. VANDERBURG (*Pharm. J. Trans.* [3], **11**, 189).—The inorganic ingredients of light-coloured Lofodin cod liver oil were determined—first, the acids, phosphoric and sulphuric, by saponification, and after separation of the fatty acids, as ferric phosphate and barium sulphate; secondly, the bases, lime, magnesia, and soda, by carbonising the oil, treating the residue with hydrochloric acid, separating the phosphoric acid from the solution and estimating lime as oxalate, the magnesia as magnesium ammonium phosphate, and the soda as sulphate. In this way 0.37805 per cent. inorganic matter was found.

P_2O_5 .	SO_3 .	CaO .	MgO .	Na_2O .
0.09135	0.07100	0.15150	0.00880	0.05540

By direct incineration of 35 grams of oil no appreciable quantity of ash was left.

By igniting English oil, 0.002 per cent. of ash was left, consisting chiefly of iron, whilst De Jongh's leaves 0.009 per cent. of ash, consisting of iron and calcium.

The results do not agree with those of De Jongh's.

L. T. O'S.

Elementary Analysis of Organic Salts of Alkalis and Alkaline Earths. By H. SCHWARZ and P. PASTROVICH (*Ber.*, **13**, 1641—1643).—The salts are mixed with pure chromic oxide and burnt in a platinum boat in a current of oxygen, the combustion tube being charged with copper oxide. Carbon and hydrogen are obtained as usual, whilst the contents of the boat are exhausted with water, and the chromate formed titrated with standard lead solution. Test experiments gave very satisfactory results.

Nitro-compounds should be mixed with chromic oxide and copper oxide.

O. H.

Analysis of Iodine-Iron Cod Liver Oil. By E. A. VANDERBURG (*Pharm. J. Trans.* [3], **11**, 189—190).—The iron may be determined by igniting 20 grams of oil in a platinum dish, which should not be more than one-sixth full. The oil should be gently heated until the colour changes to a brownish-red, when combustible gases are evolved, which may be ignited, and will continue to burn for some time. When the burning ceases, the oil is again heated until more inflammable gases are given off, which are treated as before. As soon as the oil is completely carbonised, the residue is strongly ignited until all the carbon is consumed, and the ash consisting of ferric oxide is then weighed. That the ash consists of pure ferric oxide, may be subse-

quently tested by reduction with zinc and sulphuric acid, and titration with potassium permanganate. The weight of ash multiplied by 0.7 gives the quantity of iron in the oil; it should amount to 0.27 per cent.

To determine the iodine, 5 grams of oil are saponified with alcoholic potash, the soap carbonised, and the residue washed with water. The iodine in the solution is estimated as palladium iodide.

L. T. O'S.

Testing of Mustard Oil. By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], 11, 472—473).—Mustard oil is frequently adulterated with carbon bisulphide, and therefore it is of great consequence to be able to readily detect its presence. This may be done by distilling the oil at a low temperature, when the carbon bisulphide passes over, and may be converted into ammonium thiocyanate by treatment with alcoholic ammonia. A better way of treating the distillate, if the quantity obtained will allow of its being adopted, is to take its boiling point and specific gravity, since in presence of ammonia, mustard oil decomposes to a small extent, traces of ammonium thiocyanate being formed.

The principal compound formed by the action of ammonia on mustard oil, namely, thiosinamine, $C_4H_8N_2S$, may be used to determine the value of the mustard oil. A weighed quantity of the oil is treated with alcoholic ammonia until the smell of mustard oil has entirely disappeared. The solution is then evaporated to dryness and weighed. A moderate heat must be used in order to reduce the quantity of ammonium thiocyanate formed to a minimum.

Mustard oil when exposed to the direct rays of the sun darkens in colour, and a brown deposit forms. The oil then gives a red colour with ferric chloride, and the compound thus formed is insoluble in ether, it is therefore not due to the presence of thiocyanic acid.

When the formation of xanthic acid is used as a test for the presence of carbon bisulphide in mustard oil, care must be taken that all traces of the oil are removed, as its presence may lead to deceptive conclusions, unless very dilute alcoholic potash is used in the reaction.

Pure mustard oil exposed to diffused sunlight undergoes no change. If, however, it contains carbon bisulphide, the colour changes to a very dark brown, and a dirty brown-red deposit is formed.

L. T. O'S.

Technical Chemistry.

A Photo-electric Regulator for Painted-glass Furnaces. By R. GERMAIN (*Compt. rend.*, **91**, 688--690).—The muffle in which the glass is heated is provided with a window of very refractive alumina glass, so that the red glow within may reach a distant mirror. This mirror concentrates the rays on a sphere of selenium, and the modification in the electric conductivity of that substance thus induced acts on a mechanical arrangement, whereby the fire bars are withdrawn, and the fuel allowed to fall out as soon as the right temperature to fuse the enamels is attained.

R. R.

Disinfecting Power of the Chlorphenols. By C. O. CECHE (*J. pr. Chem.* [2], 22, 345—347).—It has often been noticed that the addition of bleaching powder to carbolic acid in dressing wounds causes healing to take place more rapidly than when the acid is used alone. It has been shown by Diamin that phenol and bleaching powder react on one another, forming mono-, di-, and tri-chlorophenol, which may be isolated and separated by treatment with a strong acid, and distillation with aqueous vapour. The author, considering that these chlorophenols are probably formed when carbolic acid and bleaching powder are used together in dressing a wound, and exert a healing power greater than that of carbolic acid alone, attempted to prepare chlorophenols in quantity by the above process; it proved dangerous on the large scale, and direct treatment of phenol by chlorine gas was resorted to. A red crystalline mass was obtained, from which white crystals are obtainable by pressure between filter-paper; after purifying these crystals by precipitation from their alcoholic solution by water, they were dissolved in alcohol, and the bandages were impregnated with this solution. These crystals consist of a mixture of three chlorophenols, in which trichlorophenol predominates, and is probably the most useful. The chlorophenols present the advantage over phenol of being less corrosive and poisonous, and trichlorophenol probably has most advantage in these respects: its value as a disinfectant remains to be decided by the use of the chlorophenol bandages.

F. C.

Wickerheim's Preservative Fluid. By H. STRUVE and O. JACOBSEN (*Bied. Centr.*, 1880, 613—615).—This fluid is made by mixing together 100 c.c. water, 40 c.c. glycerol, 10 c.c. methyl alcohol, 3.33 grams alum, 0.40 gram saltpetre, 2 grams potash, and 0.66 gram arsenious oxide. In the place of alum and potash, an equivalent quantity of potassium sulphate is recommended.

J. K. C.

Action of Soda on Cast-iron. By H. BRUNCK and C. GRAEBE (*Ber.*, 13, 725—726).—A cast-iron vessel which was used for fusing soda at a red heat, was in the course of time converted into a friable mass, composed of minute crystalline scales of sp. gr. 2.92. The crystals have the composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, but contain about 1.7 per cent. of Mn_2O_3 .

W. C. W.

New Method of Fermentation. By M. DELBRÜCK and G. HEINZELMANN (*Bied. Centr.*, 1880, 622—624).—As the use of thick mashes for fermentation is attended with the development of too high a temperature, the authors recommend that the process should be commenced at about 19° or 20° R., and that the temperature of the mash be kept from rising too high by means of cooling apparatus. The time saved in this way is considerable.

J. K. C.

Mashing of Grapes. By E. MACH and PORTELE (*Bied. Centr.*, 1880, 619—620). In this investigation, a small incision was made in each grape, and the fleshy core was pressed out, the liquid which ran off at the same time was kept separate, as also the liquid which could

be pressed out of the skins. It was found that the first contained the greatest quantity of acid and cream of tartar, and the least amount of sugar, the liquid running off being richest in sugar, and yielding the strongest must.

J. K. C.

Saccharine Matters in the Fruit of the Coffee Plant. By BOUSSINGAULT (*Compt. rend.*, **91**, 639—642).—The dried fruit of the coffee plant contains:—Mannite, 2·21; inverted sugar, 8·73; cane-sugar, 2·37. From this it will be seen that the amount of sugar present in the fruit is too small to enable it to be profitably utilised as a source of alcohol, although the readiness with which it ferments had suggested that idea to Humboldt.

R. R.

Action of Animal Charcoal in the Sugar Manufacture. By H. PELLET (*Ann. Chim. Phys.* [5], **20**, 89—95).—Alkaline nitrates and chlorides are but little absorbed by animal black, but caustic lime on the contrary is absorbed in large quantity; the question which presented itself was whether lime salts were absorbed to the same extent as lime in the free state. Various solutions were made containing in different proportions sugar, calcium glucosate, potash, lime, and alkaline salts; these having been carefully analysed beforehand, were submitted to the action of purified animal charcoal at a temperature of 90—95° for a short time, and after filtration were reanalysed. The actual results are given in a series of tables, of which the following may be taken as a fair summary:—

That lime salts can be absorbed in certain proportion by animal black.

That free potash can also be absorbed by the black, and that its presence considerably augments the proportion of lime salts absorbed; in the latter case a larger proportion of potash itself is taken up.

That the presence of free lime does not sensibly modify the action of potash as far as regards the absorption of lime salts by the black.

That free lime is almost wholly absorbed, the presence of sugar being without influence on the action.

When there exists simultaneously free and combined lime in a solution, animal black absorbs the same proportion of the free lime, whilst its absorptive power for the saline lime is considerably diminished.

The presence of sugar and foreign salts generally affects the absorptive power of animal black but little.

An investigation into the alkalinity of new charcoal and of charcoal which had been used and calcined several times, showed that whilst a fresh black had an alkalinity of more than 0·15 per cent. (returned as lime), an old sample contained only 0·05 per cent., or not one-third that in a new one; as a necessary consequence, therefore, and from a consideration of the foregoing experiments, a new black should absorb a larger proportion of lime salts than an old one; in actual practice such is always found to be the case.

J. W.

Inversion of Sugar during Manufacture. By DURIN (*Bied. Centr.*, 1880, 618—619).—According to the author, this is due to the

oxidation, and consequent acidification of the sugar during the process of manufacture, and can be avoided by the use of a small quantity of alkali.

J. K. C.

Separation of Sugar from Molasses. By JÜNEMANN and C. SCHEIBLER (*Bied. Centr.*, 1880, 687—688).—The method of Jünemann consists in the precipitation of sugar by means of lime in hot solution and washing the precipitate under pressure at 172°; according to Scheibler, however, this method presents difficulties which make it unsuccessful in practice.

J. K. C.

Manufacture of Vinegar by Means of Bacteria. By E. WURM (*Pharm. J. Trans.* [3], 11, 132—134).—According to Pasteur, the formation of vinegar from alcohol is due to the vegetation of the bacterium, *Mycoderma aceti*. Liebig, however, maintained that it is due to chemical and not physiological action, since no *Mycoderma aceti* could be detected by microscopic examination on a shaving from the bottom of a vinegar generator which had been in use for 25 years. Mayer and De Knierym, however, distinctly proved that the ferment exists in great quantity on the shavings of the vinegar generator.

The author has carried out the manufacture according to the directions of Pasteur, and most satisfactory results have been obtained. 200 liters of a mixture of alcohol, water, and vinegar, with mineral salts, namely, potassium phosphate, 0·01 per cent.; calcium phosphate, 0·01 per cent.; magnesium phosphate, 0·01 per cent.; ammonium phosphate, 0·02 per cent., are placed in a large wooden vat well closed with a wooden cover, access to air being obtained through small openings at the side. The mycoderma are sown by means of a wooden spatula. The liquid in the vats is maintained at 25—30° C., and the temperature of the surrounding atmosphere at about 30° C. Pasteur limits the amount of vinegar to 1 per cent., but a liquid so slightly acid is easily invaded by *Saccharomyces mycoderma*, which hinders the generation of the acetic fungus. Experiments prove that with from 0·5—1·2 per cent. of acetic acid present, the *Saccharomyces mycoderma* multiply exclusively; with 1·6 per cent. the *Mycoderma aceti* predominate, and with 2 per cent. the latter alone multiply.

The liquid in the vat originally contained 2 per cent. of alcohol, and as this is converted into vinegar fresh quantities are added, until the vinegar has attained the required strength. When the surface of the vat becomes entirely covered with bacteria, the surrounding temperature being 30° C., that of the liquid rises to 34° C., and a strong odour of acetic acid is apparent. The augmentation of the acid varies from 0·2—2·4 per cent. daily. The loss of alcohol in this process is much less than in the generators with shavings, which in the preparation of crude vinegar amounts to 23 per cent., but in the case of stronger vinegar 12 to 15 per cent. In this process, however, there is only loss from evaporation at the beginning, it being afterwards prevented by the layers of fungus. The total loss is from 10 to 15 per cent., one portion of which is used by the bacteria in forming their substance, and the other converted into ethyl acetate at the high temperature of the solution.

An addition of alcohol should not be made when there is more than 0.5 per cent. in the vat, and it should be added in such a way that the liquid coming in contact with the fungus does not contain more than 0.5 per cent. The greater proportion of acid in the liquid, the more nearly should the quantity of alcohol added equal the quantity used up.

When the vinegar has reached the required strength, it is drawn off into vats, where it is clarified and freed from mycoderma.

The precautions to be observed are—the sowing of pure bacteria, a uniform temperature of 30°, and a well regulated addition of alcohol. The chief advantages of this process are its cheapness and the great economy of space, and a much greater yield.

The generation of “vinegar eels” is of great inconvenience, since by their motion they destroy the pellicle of the mycoderma, and prevent its reforming. If they multiply to any great extent, the temperature of the liquid falls, but by preventing the cooling, the parts of the pellicle destroyed may be reproduced, in which case the eels take refuge in the upper parts of the vessel, and form a ring of viscosity above the layer of bacteria. In this process, however, they have not time to multiply so as to become injurious, since the vats are emptied every 10–14 days. The mycoderma used for sowing must not come from a liquid infected with eels.

The microscopic examination of the ferment shows that three different forms can be observed. Whether they are from the same organism in different stages of development, or three different organisms capable of producing acetic acid, remains to be proved.

With 1 to 3 per cent. of acetic acid the formation of a thick viscous and fatty skin was observed, consisting of minute globules (micrococci), occurring whilst young in contiguous rows, but after a few days changing into an animal glue, through the formation of intercellular tissue. An increase in the quantity of acid caused the formation of veins, rays, and spots which extend more and more, whilst the original layer sinks to the bottom. This new pellicle consisted of bacilli, and was less viscous than the first. It, however, became more viscous, and was replaced by a more delicate pellicle of bacilli. The amount of 1 per cent. of acid is sufficient to stop the production of the micrococci, but in such a mixture the bacilli continue to multiply. No difference has been as yet detected in the power of acetification of these two forms. Thin pellicles should be taken for sowing, as they germinate more quickly than the viscous pellicles.

L. T. O'S.

Apparatus for Skimming Milk. By C. STIMMEL (*Bied. Centr.*, 1880, 617–618).—The cream is allowed to rise in shallow pans, immersed in cold water, and the milk separated by means of a syphon.

J. K. C.

Colouring Matter of *Rubus Chamaemorus*. By C. O. CECH (*J. pr. Chem.* [2], 22, 399–400).—The author noticed that the cotton and woollen bags in which the berries of this plant were subjected to pressure to obtain their juice for making wine were coloured intensely orange-yellow. The colour imparted was so per-

manent and had so thoroughly penetrated the fibre, that it was unaffected even by dilute hydrochloric acid.

Experiment showed that the juice of these berries imparted an intense orange-red colour to cotton and wool in a few minutes, and somewhat more slowly to silk.

The colouring matter appears to be present in considerable quantity, and the author is now engaged in isolating it.

Its colour will be suitable for dyeing shades of chamois amber and orange-yellow, and also for harmlessly colouring white wines in imitation of sherry.

F. C.

Coccus Red. By R. ROTHER (*Pharm. J. Trans.* [3], 11, 130).—There being several defects in the usual method for the preparation of coccus red, the author has submitted a new process. Two parts of sodium chloride are dissolved in a mixture of 1 part of hydrochloric acid and 44 parts water, and 8 parts of cochineal are macerated in the solution for two days; after which time the solution is decanted and the residue again digested with 32 parts water for two days. This solution is then poured off, and the residue digested with 32 parts water, containing 3 parts sodium chloride in solution; and after two days the mixture is strained and subjected to strong pressure. The three solutions are mixed, and the clear solution decanted from the sediment. In the decanted liquor 2 parts alum are dissolved, and 2.5 parts ammonia solution (16 to 18 per cent.) added, and the resulting precipitate is collected and washed free from ammonium salts, and finally dissolved in a warm solution of sodium citrate (prepared by neutralising 1 part of citric acid with sodium carbonate). The solution is diluted with water to 28 parts, and mixed with 4 parts alcohol. The principle of this process is first to extract the dibasic carminic acid, then unite it with aluminium, and finally to bring the aluminium salt into solution. The dry compound may be obtained by precipitating the concentrated solution with alcohol, or allowing it to evaporate slowly.

The aluminium carminate obtained by precipitating the acid with alum and ammonia is a dark purple-red powder, soluble in acids to a scarlet solution, and in alkalis to deep purple. Acid solutions of a carminate, when diluted with large quantities of water, change from bright scarlet to purple or deep pink; dilution with alcohol does not produce the same effect. Aluminium carminate is also soluble in aluminium citrate, with a purple colour.

Coccus red may also be obtained by treating ammonium carminate with aluminium citrate.

By treating some of the crude solution with aluminium hydrate, precipitated with ammonia, no result was obtained. On adding acetic acid to the mixture, a solution was obtained from which alkaline carbonates failed to give a precipitate. On adding calcium carbonate, however, a gelatinous greenish-black magna was obtained, slightly soluble in water, soluble in acids to scarlet solutions, and in alkalis to purple. Lime water changes its colour to pink. It is slowly decomposed by ammonium sulphate, and quickly by aluminium sulphate, giving a purple solution, the colour of which is not destroyed by

alcohol. On spontaneous evaporation, a purple crystalline residue is obtained.

The filtrate from the calcium salt is of a purple colour, and from it ammonia throws down a pink precipitate, leaving a light scarlet solution. Barium and magnesium compounds corresponding to the calcium compound could not be obtained.

L. T. O'S.

Analysis of Bohemian Tea. By BELOHOUBECK (*Bied. Centr.*, 1880, 703).—So-called Bohemian tea, the leaves of *Lithospermum off.*, is often used to adulterate ordinary tea. Compared with Chinese tea, it yields the following figures on analysis:—

	Bohemian tea.	Chinese tea.
Cellulose	5.96	21.30
Tannin	8.25	13.78
Fat	9.29	3.76
Ethereal oil	—	0.67
Other nitrogen-free organic bodies	26.49	24.12
Thein	—	1.76
Albumin	24.54	19.90
Water	9.85	9.32
Ash	20.59	5.34

J. K. C.

Preparation of Iodine-iron Cod Liver Oil. By S. D. VON VALAENBURG (*Pharm. J. Trans.* [3], 11, 209).—1.25 parts of iodine are dissolved in 98.5 parts of cod liver oil by constant shaking and stirring. The solution, having the sp. gr. 0.932—0.937, is poured into a vessel, which is hermetically closed and shaken with 2.5 parts iron until it assumes a purple colour, and contains no free iodine. This is ascertained by shaking a portion of the oil with a solution of potassium iodide and starch-paste. The mixture is then allowed to stand for 24 hours, then shaken again, and finally allowed to stand until clear. The clear liquid has the sp. gr. 0.937—0.94, and should contain 1.23 per cent. iodine and 0.27 per cent. iron. In the preparation, air should be excluded as much as possible, since it causes the quantity of iron to increase, owing to the formation of ferric oxyiodide.

French iodine is generally used in preference to English, since the latter, on account of its fineness, forms a tough mass when mixed with the oil, and this can only be broken up with difficulty. In some cases, a dark-coloured amorphous substance adheres to the bottom of the vessel; it is insoluble in ether, and can be almost completely volatilised.

The mixture, although originally containing no free iodine, is found to contain it after standing for 24 hours, owing to the formation of a small quantity of ferric iodide, which, on standing, is decomposed into ferrous iodide and iodine. The violet colour is due to the presence of ferric oxyiodide. The mixture readily oxidises on exposure to the air, losing its colour.

Water destroys the mixture, since it first dissolves the ferrous iodide, which it afterwards decomposes.

L. T. O'S.

Steeping Hemp. By A. RENOUARD (*Bied. Centr.*, 1880, 630).—The water in which hemp has been steeped produces no evil effects on the health of a district when allowed to flow into running water, but it always destroys the fish, together with certain vegetable growths.

J. K. C.

Hardness and Resistance of Wood. By V. NÖRDLINGER (*Bied. Centr.*, 1880, 600—602).—The resistance of wood is greatest when it has been cut in May or October; this is especially the case with young trees.

J. K. C.

A Baking Powder. By M. WEITZ (*Bied. Centr.*, 1880, 389—390).—The report of an examination of a baking powder which has been selling freely in Berlin. It consists of fine wheat flour, with a small addition of inorganic matter, which, when water is added, disengages gas, and renders the dough porous, acting as a substitute for yeast. This preparation has been found well adapted for the purpose. The gas is carbonic anhydride, and each kilogram of the powder contains 5.1 gram of phosphoric anhydride and 8.7 grams of sodium bicarbonate. It is very similar to the proportions recommended for baking powder by Liebig, except that he recommended the ingredients to be kept separate until required for use.

J. F.

Preservation of Fruit in Winter. By P. SARAUER (*Bied. Centr.*, 1880, 383—385).—The object of preserving fruit in their fresh state is best attained by keeping them in a cool dark place. The author's experiments were directed so as to ascertain the influence of dry and damp air on the stored fruit. Apples were the subjects of his investigation. They were kept in an ordinary fruit store, part exposed to damp air in the open store, part enclosed in glass vessels, through one of which dry and the other damp air was aspirated. The loss of weight per cent. was: loose samples, 3.42; dry air, 7.90; saturated with damp, 0.60. The sample which was in dried air did not show mould so soon, but it shrivelled quickly and ripened, and at the end of the experiments tasted less sweet, and showed a larger proportion of decayed fruit. The breaking off or leaving on of the stalk has a considerable effect on the drying out of the moisture; leaving it on promotes a rapid evaporation. The removal of the external coating of wax by means of ether, &c., also promotes rapid evaporation. Wrapping the apples in silk paper was not found to be advantageous, except when the storing place was unusually dry; the germs of mould attacked the rough portions of the fruit with great avidity through the openings in the paper. Packing in straw was also found injurious, the least dampness in the straw imparting a musty flavour to the fruit. Dry sand is recommended strongly above all other means of preserving fruit. The specimens tried by the author would apparently have kept fresh and sweet until the July of the following year. The loss of weight was not half that of the loose fruit; there was no appearance of mould, and the damaged specimens did not infect their neighbours. The chief point in selecting fruit for preservation is to choose those with whole sound skins and with the waxy covering perfect.

J. F.

General and Physical Chemistry.

Evaporation without Fusion. By L. MEYER (*Ber.*, **13**, 1831—1833).—The author (*Ber.*, **8**, 1627), has shown that the conversion of a solid body directly into the gaseous or indirectly through the liquid state is dependent on the pressure. If iodine is melted in an exhausted tube, and the heat raised until the maximum tension of the vapour at the melting point is reached, the iodine melts in a black stream along the side of the tube. On cooling, the fluid iodine begins to boil, and then solidifies; on warming again, the solidified mass of iodine exhibits Leidenfrost's phenomenon. The same is observable with Japan camphor, naphthalene, anthracene, and hexachlorethane. Carnelley has defined that pressure below which no amount of heat will melt a substance, as the "critical pressure," a term analogous to Andrew's "critical temperature." But these definitions are not strictly comparable, for by the pressure on the substance is meant the pressure of its own vapour. In order that these definitions may be compared they must be as follows:—

The critical temperature of a gas is that above which no pressure can liquefy it.

The critical pressure of a solid is that tension of its own vapour under which no increment of heat can melt it.

V. H. V.

Lothar Meyer and the latest Discovery in Physics. By O. PETTERSSON (*Ber.*, **13**, 2141—2144). This is a criticism on Lothar Meyer's remarks (*Ber.*, **13**, 1831) in reference to the results recently published by Carnelley (*Nature*, Sept. 8th, 1880) on the critical pressure of substances, and the existence of bodies at temperatures considerably above their ordinary melting points. In conclusion, it is pointed out that the existence of bodies above their ordinary melting points when heated under low pressures depends on the same principle as the lowering of the melting point by increased pressure, as was predicted by Prof. J. Thomson, and confirmed by Sir W. Thomson and others.

T. C.

Lecture Experiment. By R. HAASS (*Ber.*, **13**, 2203).—This is an experiment to illustrate the critical pressure of a substance as recently described by Carnelley (*Chem. News*, **42**, 130). A solid piece of mercuric chloride is introduced into a glass tube closed at one end, and connected at the other with an air-pump; on reducing the pressure below about 400 mm. it is impossible to melt the salt, however strong the heat applied, the solid merely subliming into the cooler portions of the tube; on letting in the air fusion begins when the pressure has risen to about 450 mm.

T. C.

Note.—This experiment as far as it goes is identical with that
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shown by Carnelley at the Chemical Society on Dec. 16th, 1880, and described in a paper received by the Royal Society on Nov. 11th.

Reciprocal Displacement of the Halogens in absence of Water. By M. POTILITZIN (*Bull. Soc. Chim.* [2], **34**, 220—225).—From the author's previous researches (*ibid.* [2], **27**, 303, it would appear that bromine replaces chlorine in the anhydrous metallic chlorides, and that when equivalent quantities act on one another the percentage of halogen replaced depends on the atomic weight and quantivalence of the metal, and on the temperature. For two bodies in the same system, the percentage of halogen replaced increases with the mass (number of molecules of bromine entering into the reaction). The author has repeated and extended his previous experiments, finding that the limit of change between a given system of two bodies, such as $\text{BaCl}_2 + \text{Br}_2$, is attained in a few hours at 400° ; in the case quoted from 2—6 hours. By arranging the elements according to Mendelejeff's periodic law in a table showing the percentage of chlorine replaced by bromine in their chlorides, it is seen that in the same vertical series the amount of chlorine replaced is proportional to the atomic weight of the element, and therefore in that series $\frac{A}{p} = \text{constant}$, where A = atomic weight of the metal, and p the percentage of chlorine replaced:—

$\text{RCl} + \text{Br}$.		$\text{RCl}_2 + \text{Br}_2$.		$2\text{RCl}_3 + 3\text{Br}_2$.		$\text{RCl}_4 + 2\text{Br}_2$.		$\text{R}_2\text{Cl}_6 + 3\text{Br}_2$.	
	Percentage of chlorine replaced.		Percentage of chlorine replaced.		Percentage of chlorine replaced.		Percentage of chlorine replaced.		Percentage of chlorine replaced.
$\text{LiCl} \dots$	1.84	CaCl_2	2.5	—	—	—	—	—	—
$\text{NaCl} \dots$	5.56	SrCl_2	5.21	—	—	—	—	—	—
$\text{KCl} \dots$	9.78	BaCl_2	7.78	—	—	—	—	—	—
$\text{AgCl} \dots$	27.28	HgCl_2	12.02	—	—	SnCl_4	1.49	Fe_2Cl_6	0.72
—	—	PbCl_2	12.43	BiCl_3	5.38	—	—	—	—
Mean constant $\frac{A}{p}$	} 3.98	16.71		38.66		79.19		155.55	

In comparing elements in the same horizontal series* it is seen that the percentage of chlorine replaced diminishes as the quantivalence of the element increases, not progressively, but as the square of the valency; hence $\frac{A}{pE^2} = \text{constant}$ (4 nearly) where E = the quantivalence of the element.

* The horizontal series in the table are not identical with those of Mendelejeff's.

From further considerations the author is of opinion that the fixed limit arrived at in these reactions with anhydrous bodies, whether they be accompanied with the evolution or absorption of heat, is a function of the atomic weight, the mass of the acting bodies, and the temperature; this has been proved to be true for bodies in solution.

In discussing the thermochemical results on the separation of acids and bases, the author shows that in cases where the amount of chemical energy developed is but small, it is doubtful whether the calorimetric method can be employed. This applies to these reactions, since in the reciprocal actions of the bodies the rapidity of the formation of the molecules (the rapidity of the reaction) ought to diminish, as the limit of reaction is reached; this has been confirmed by the results of Malaguti, Guldberg, Harcourt, and others. Consequently the work measured by the calorimetric method, as the total transformation of one system into another, is only the work done in the first five or ten minutes of the reaction; and therefore the thermochemical results are only proportional to the rapidity of the reaction in those first moments; and the so-called thermal equivalents, although pointing out the direction of the principal reaction, do not measure the affinities, nor foretell or explain the number of inverse reactions accompanied by an absorption of heat. In these considerations may be found an explanation of the divergence between the predicted and experimental thermochemical results.

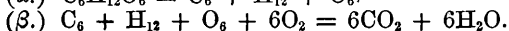
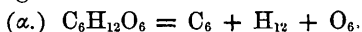
L. T. O'S.

Heat of Combustion of Benzene. By J. THOMSEN (*Ber.*, **13**, 1806—1807).—The author remarks on the importance of heat determinations of benzene as the foundation of the aromatic compounds. The heat of combustion of a molecule (72 grams) of benzene vapour was found to be 805,800 heat-units. As the heat of formation is equal to the difference between the heats of combustion of the constituents of the compound and of the compound itself, the following values are deduced:—

Heat of combustion of benzene vapour.	Heat of combustion of constituents. { (CO ₂) = 96,960 h. u. (H ₂ O) = 68,360 h. u.	Heat of formation of gaseous benzene.	
		At constant pressure.	At constant volume.
805,800 h. u.	786,840 h. u.	— 18,960 h. u.	— 20,120 h. u.

V. H. V.

Heat of Combustion of Carbon Compounds. By C. v. RECHENBERG (*J. pr. Chem.*, **22**, 1—45).—The following is a summary of the author's results. In all cases the products formed were CO₂ (gaseous) and H₂O (liquid), and Berthelot's values for these were adopted in the calculations, viz., C + O₂ = CO₂ = 94 cal., and H₂ + O = H₂O = 69 cal. The combustion of dextrose affords an example of the method of calculation. The process may be resolved into two stages:—



The amount of heat evolved in these two processes is + 709 cals. The heat evolved in (β) is, however, equal to the sum of the heat of formation of 6 mols. CO_2 and 6 mols. of H_2O , i.e., $564 + 414 = +978$, therefore the heat of (α) must be $709 - 978 = -269$. Then as -269 represents the heat of decomposition of dextrose into its elements, it must also represent the heat of its formation from its elements.

The following table gives the values for the compounds experimented on, "cal" being the heat necessary to heat 1 kilo. of water 1°C ., and c the amount necessary to heat 1 gram :—

Name.	Formula.	Molecular weight.	Heat of combustion of		Heat of formation.
			1 gram c.	1 mol. cal.	
Dextrose anhydride.....	$\text{C}_6\text{H}_{12}\text{O}_6$	180	3939	709	+ 269
Dextrose hydrate.....	$\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$	198	3567	701	+ 346
Lactose anhydride	$\text{C}_6\text{H}_{12}\text{O}_6$	180	3894	701	+ 277
Cane-sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	342	4173	1427	+ 460
Maltose anhydride	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	342	4163	1424	+ 476
Maltose hydrate	$\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$	360	3932	1416	+ 540
Milk-sugar anhydride.....	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	342	4162	1423	+ 464
Milk-sugar hydrate.....	$\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$	360	3945	1420	+ 536
Starch	$\text{C}_6\text{H}_{10}\text{O}_5$	162	4479	726	+ 183
Erythrodextrin	$\text{C}_6\text{H}_{10}\text{O}_5$	162	4325	701 [?]	+ 208 [?]
Inulin	$\text{C}_6\text{H}_{10}\text{O}_5$	162	4398	712	+ 197
Cellulose	$\text{C}_6\text{H}_{10}\text{O}_5$	162	4452	721	+ 188
Metarabic acid.....	$\text{C}_6\text{H}_{10}\text{O}_5$	162	4464	723	+ 186
Mannitol	$\text{C}_6\text{H}_{14}\text{O}_6$	182	4175	760	+ 287
Dulcitol.....	$\text{C}_6\text{H}_{14}\text{O}_6$	182	4135	753	+ 294
Myristic acid	$\text{C}_{14}\text{H}_{28}\text{O}_2$	228	9540	2175	+ 107
Stearic acid	$\text{C}_{18}\text{H}_{36}\text{O}_2$	284	9886	2808	+ 126
Oxalic acid	$\text{C}_2\text{H}_2\text{O}_4$	90	659	59	+ 198
Malonic acid.....	$\text{C}_3\text{H}_4\text{O}_4$	104	1992	207	+ 213
Succinic acid	$\text{C}_4\text{H}_6\text{O}_4$	118	2996	354	+ 229
Tartaric acid.....	$\text{C}_4\text{H}_6\text{O}_6$	134	1408	211	+ 372
Citric acid.....	$\text{C}_6\text{H}_8\text{O}_7$	148	2531	486	+ 354
Phenol	$\text{C}_6\text{H}_6\text{O}$	94	7908	743	+ 28
Benzoic acid.....	$\text{C}_7\text{H}_6\text{O}_2$	122	6650	811	+ 54
Phenylacetic acid.....	$\text{C}_8\text{H}_8\text{O}_2$	136	7127	969	+ 59
Phthalic acid	$\text{C}_8\text{H}_6\text{O}_4$	166	4855	806	+ 153
Salicylic acid	$\text{C}_7\text{H}_6\text{O}_3$	138	5503	759	+ 106
Metahydroxybenzoic acid	$\text{C}_7\text{H}_6\text{O}_3$	138	5464	754	+ 111
Parahydroxybenzoic acid	$\text{C}_7\text{H}_6\text{O}_3$	138	5448	752	+ 113
Naphthalene.....	C_{10}H_8	128	9831	1258	- 42
Anthracene	$\text{C}_{14}\text{H}_{10}$	178	9977	1776	- 115
Anthraquinone.....	$\text{C}_{14}\text{H}_8\text{O}_2$	208	7198	1424 [?]	+ 168 [?]

The conclusion will follow.

G. T. A.

Determination of the Densities of Permanent Gases. By V. MEYER (*Ber.*, 13, 2019—2021).—For the determination of the density of the permanent gases at high temperatures, the author has devised an apparatus which consists of a pipette-shaped vessel (of about 100—200 c.c. capacity) fitted with two capillary tubes at each end. The apparatus is filled with the gas, which, after acquiring the temperature of the vessel, is expelled by another having no chemical action on it. The expelling gas and the method of performing the experiment is varied according to circumstances; thus if the gas is insoluble in water, it may be expelled by carbonic or hydrochloric acid and measured over water or potash. Before and after an experiment the apparatus is filled with air or nitrogen and expelled by carbonic or hydrochloric acid and measured over water, the expelled volumes of air or nitrogen will be equal if the temperature has remained constant. By a comparison of the air collected on the one hand, and of the gas on the other (under the same conditions), the density of the gas at the higher temperature is determined, without necessarily ascertaining the pressure or temperature to which it has been subjected. At higher temperatures a similar shaped apparatus, made of porcelain or platinum, is used, and instead of the capillary tubes the vessel is partly closed at each end by glass or graphite stoppers so as to allow a minute annular space between the stoppers and the vessel. By means of this apparatus the author, in conjunction with H. Züblin, has established that hydrogen undergoes no change in density at the highest temperature of a Schloësing's oven. A table is given of those gases whose expansion-coefficient is unaltered even at very high temperatures. V. H. V.

Volume Constitution of Sulphates, Chromates, and Selenates. By H. SCHRÖDER (*J. pr. Chem.* [2], 22, 432—460).—A continuation of the previous paper of the author on this subject (*J. pr. Chem.* [2], 19, 267; this Journal, 1879, Abstr., 768; see also this Journal, 1878, 926). The molecular volumes of the anhydrous sulphates, chromates, and selenates of potassium, silver, glucinum, and cæsium are multiples of 5.52, as are also the volumes of the anhydrous sulphates of magnesium, zinc, copper, cobalt, iron, manganese, and nickel. In the case of the sulphates of ammonium, rubidium, and thallium, the molecular volumes must be doubled in order to become multiples of 5.52. A large number of molecular volumes of sulphates, selenates, and chromates containing water of crystallisation are then discussed. It appears that water may have two different molecular volumes, and that the number of molecules occupying the more condensed volume in these salts stands in no direct relation to the chemical composition; it amounts to 1, 2, $2\frac{1}{2}$, and 3 mols., and cannot be referred to the nature of the acid and base merely, but is most directly influenced by the nature and temperature of preparation. The author points out that the stere, 5.52, must be taken only as a first approximation to the truth; that the stere of the selenates is slightly greater than that of the sulphates, and the stere of an ammonium compound slightly greater than that of the corresponding potassium compound. A. J. G.

History of Periodic Atomicity. By D. MENDELEJEFF (*Ber.*, **13**, 1796—1804).—In this paper the author claims priority for the publication of the law of periodic atomicity in answer to Lothar Meyer (*Ber.*, **13**, 259). The author considers that Carnelley (*Phil. Mag.*, October to December, 1879) has added the only new facts to this theory since the original publication in the *Journ. Russ. Chem. Soc.* The author also states that he is not indebted for his theory to Newlands or Lothar Meyer, but only to Lenssen and Dumas. A freshly-arranged table of elements is given. V. H. V.

Periodic Atomicity. By L. MEYER (*Ber.*, **13**, 2043—2044).—An answer to Mendelejeff's communications (*Ber.*, **13**, 1796).

Inorganic Chemistry.

Preparation of Hydrochloric Acid Gas. By L. L. DE KONINCK (*Zeits. Anal. Chem.*, 1880, 467—468).—The author prepares hydrochloric acid by the action of concentrated sulphuric acid on ammonium chloride, the advantage of the method consisting in the regularity of the action, and in the residue of ammonium sulphate being non-crystalline and syrupy. O. H.

Action of Iodine on Phosphorus Trichloride. By C. G. MOOT (*Ber.*, 13, 2029—2031).—On mixing iodine with phosphorus trichloride, the liquid is reddened and a part of the iodine is dissolved. On exposing the liquid to moist air, a golden substance separates out; the author establishes that moisture, and not the oxygen of the air, is necessary for this change. On treatment of a small quantity of phosphorus trichloride with a large excess of iodine, a solid mass is obtained completely soluble in carbon bisulphide; on evaporating the solution, fine red hexagonal crystals of the formula PCl_3I , separate out, which are decomposed by moist air, and split up with liberation of iodine when heated.

The author promises a further account of the properties of the golden substance and of phosphorus trichloriodide. V. H. V.

Impurities in Sodium Bicarbonate. By A. KOSTER (*Arch. Pharm.* [3], 14, 31—33).—Ammonium bicarbonate may occur to the extent of nearly 4 per cent. in sodium bicarbonate prepared by the ammonia process. O. H.

Action of Hydrochloric Acid at High Temperatures on Ultramarine rich in Silica. By P. G. SILBER (*Ber.*, 13, 1854—1857).—The author considers that all previous analyses of red ultramarine were of specimens contaminated with blue ultramarine (R. Hoffmann, this Journal, Abstr., 1879, 108). By the action of hydrochloric acid at high temperatures with access of air, a violet

ultramarine is obtained which bears the same relation to the blue and red ultramarines that the green ultramarine does to the white or blue in the series poor in silica.

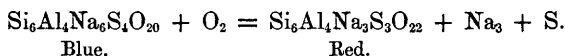
By systematic washings, the violet can be separated from the unaltered blue. By further treatment with hydrochloric acid, the violet can be converted into the red of commerce, which may be fractionally separated from the violet. The violet portion in the red of commerce is due either to an imperfect action of hydrochloric acid or to the change of red into violet after continuous treatment with water. The violet can be reconverted into the red on heating with water at 130° , or more directly by a drop of soda.

In order to obtain a perfect red, the trade product is heated with hydrochloric acid until no further change of colour is evident, the sodium chloride removed by washing with slightly alkaline water, and the completely washed product dried below 150° . If dried at a higher temperature, the red immediately passes over into the yellow ultramarine.

Analyses of Ultramarines.—*a*, a blue of greatest purity used for the preparation of the violet and red; *b* and *c*, violet and red of commerce; *d*, red from *c* after all the sodium had been separated out; and *e* (yellow), from *d* after heating for a long time in the air.

	<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>e</i> .
Si	19·07	18·91	19·39	20·51	21·44
Al ..	13·04	13·55	13·80	13·99	14·52
Na ..	15·92	14·53	11·29	8·98	8·00
S	14·09	12·39	12·44	12·14	10·90
O	37·88	40·62	43·08	44·38	45·14

From these analyses it follows that in the conversion of ultramarine-blue into yellow, half the sodium contained in the blue must be removed. The author considers that on account of the similarity of the analytical numbers of *d* and *e*, that *e* is not a pure yellow. The numbers for perfect red (*d*) correspond with the formula, $\text{Si}_6\text{Al}_4\text{Na}_3\text{S}_3\text{O}_{22}$, and the conversion of blue into red can be expressed by the following equation:—



The author proposes to study the action of hydrochloric acid on ultramarines poor in silica. V. H. V.

Atomic Weight of Glucinum. By L. MEYER (*Ber.*, **13**, 1780—1786).—According to Nilson and Pettersson (this Journal, Abstr., 1880, 792) the equivalent of glucinum is 4·55, and its atomic heat normal if the atomic weight be taken as 13·65, making glucinum a triad. The author objects to these conclusions, and considers glucinum a dyad with an atomic weight of 9·10. Firstly, if glucinum had an atomic weight of 13·65, it would have a position in the system of elements between nitrogen and carbon which would not correspond to any of the known properties of the metal; but this consideration is not sufficient to justify any correction of its atomic weight. Secondly,

Nilson and Pettersson have shown that the specific and atomic heats increase slightly with the temperature like those of iron, hence for glucinum an atomic weight of 13.65 best corresponds with the mean specific heat between 0° and 100° . But the author establishes that even adopting Nilson and Pettersson's determinations, glucinum is rather comparable with carbon, boron, and silicon, whose specific heats increase at first rapidly, then more slowly, until a limit is reached at which they show a normal specific heat. Then glucinum would be a dyad with an atomic weight of 9.1: for if glucinum has an atomic weight of 13.65, its atomic heat at 157° should be 7.10, and at 257° is 8.94, which is far greater than those of iron and silver.

V. H. V.

Atomic Weight of Glucinum. By L. F. NILSON (*Ber.*, **13**, 2035—2040).—This paper is in answer to that of L. Meyer (*Ber.*, **13**, 1780). The author points out 1st, that glucinum with the atomic weight of 9.1 departs from the regular series of Mendelejeff's classification by more than 13.75 per cent. from the number required for this system; thus of all the elements of the first series glucinum is the only one which differs from the neighbouring elements of the second series by not less than 16. 2nd. Although Meyer compares glucinum with boron, silicon, and carbon, with regard to the increase of specific heat with increase of temperature, yet in Weber's researches on these latter elements, neither pure materials, nor even compounds of known composition, were used: for Hampé has established that crystalline boron contains aluminium and carbon, and Mixter and Dana have shown that crystalline silicon contains zinc and iron. 3rd. The molecular heat of glucina and its sulphate is equal to those of alumina, scandia, gallium oxide and their sulphates (*Ber.*, **13**, 1459; *Abstrs.*, 1880, 838), but differs from those of the oxides and sulphates of magnesia, copper, and other dyad metals.

The formula G_2O_3 is then in accordance with the laws of Dulong and Petit and Naumann, and although glucinum has an atomic heat of 5.79 (between 0° and 100°), slightly less than the normal number, yet in this respect it resembles its analogues aluminium and gallium.

V. H. V.

Phosphotungstic Acid. By M. SPRENGER (*J. pr. Chem.* [2], **22**, 418—432).—Phosphotungstic acids have been previously described by Scheibler (*Ber.*, **5**, 801; this Journal, 1873, 246) who obtained acids of the formulæ $H_{16}PW_{11}O_{43}$, $18H_2O$ and $H_{11}PW_{10}O_{38}$, $8H_2O$, and by W. Gibbs (*Ber.*, **10**, 1385; this Journal, 1877, **2**, 848), who prepared an acid of the formula $20WO_3$, P_2O_5 , $8H_2O$, $x\text{Aq}$.

In the author's experiments, barium tungstate was suspended in water and mixed with dilute phosphoric acid; the resulting precipitate was then decomposed by dilute sulphuric acid in slight excess, such excess being afterwards removed by cautious addition of baryta-water. The solution is evaporated on the water-bath and finally in a vacuum: an acid is then obtained in large well-formed crystals of the regular system, which are efflorescent, readily soluble in water, and have the formula P_2O_5 , $24WO_3$, $61H_2O$. The following salts were prepared and analysed:— $3BaO$, P_2O_5 , $24WO_3$, $58H_2O$; $2BaO$, P_2O_5 ,

24WO_3 , $59\text{H}_2\text{O}$; 2BaO , P_2O_5 , 24WO_3 , $59\text{H}_2\text{O}$; BaO , P_2O_5 , 24WO_3 , $59\text{H}_2\text{O}$; 3CuO , P_2O_5 , 24WO_3 , $58\text{H}_2\text{O}$; $3\text{Ag}_2\text{O}$, P_2O_5 , 24WO_3 , $58\text{H}_2\text{O}$; Ag_2O , P_2O_5 , 24WO_3 , $60\text{H}_2\text{O}$; of these the silver salts are insoluble in water. Addition of excess of baryta to a solution of the acid causes a precipitate of barium tungstate, whilst on evaporating the solution, a salt, 7BaO , P_2O_5 , 22WO_3 , $59\cdot5\text{H}_2\text{O}$, crystallises in doubly refracting needles of the rhombic system.

A. J. G.

Sodium Arsenate. By G. FLEURY (*J. Pharm.* [5], 2, 367—368).—Sodium arsenate containing $14\text{H}_2\text{O}$ may be prepared by exposing the ordinary commercial salt to a moist atmosphere for 12 days at a temperature of $15\text{--}30^\circ$.

L. T. O'S.

Bismuth Subnitrate. By A. RICHE (*J. Pharm.* [5], 384—387).—Further analyses of specimens of bismuth subnitrate, when compared with previous results (this Journal, 34, 841), show that the commercial article contains lead, varying from 0·34 to 0·03 per cent. lead sulphate. The actual quantity of lead present, however, is only $\frac{1}{10000}$ part.

Besides lead, the subnitrate is found to contain arsenic varying from $\frac{2}{1000000}$ to $\frac{1}{100000}$ part of arsenious acid, or about 0·01 per cent. It is probable that so small a quantity of arsenic passes through the system without being absorbed. Nevertheless, the author urges the use of extra precaution in the purification of bismuth subnitrate.

The estimation of nitric acid shows that it varies from 4·52 to 0·57 per cent. N_2O_5 as compared with 16 per cent. according to the codex, proving that the commercial substance has a very different composition from that prescribed.

L. T. O'S.

Manganese Dioxide containing Antimony. By H. REINSCH (*J. pr. Chem.*, 22, 111).—The author found that, on passing sulphuretted hydrogen into the acid liquid formed in the preparation of chlorine by means of hydrochloric acid, the precipitate contained antimony. He could not ascertain where the manganese dioxide came from.

G. T. A.

Organic Chemistry.

Decomposition of Simple Organic Compounds by Zinc-dust. By H. JAHN (*Ber.*, **13**, 2107—2118).—The following compounds when passed over zinc-dust at a temperature of 300—350°, are decomposed.

Ethylic ether gives ethylene and hydrogen, together with small quantities of marsh-gas and carbonic oxide.

Formic acid gives carbonic oxide, hydrogen, and a small quantity of marsh-gas.

Acetic acid gives acetone, carbonic oxide, hydrogen, and propylene

(compare Liebig and Pelouze; also Berthelot, *Ann. Chem. Pharm.*, **81**, 114; also Trommsdorff and Chenevix).

Acetic anhydride gives acetone, propylene, carbonic oxide, and hydrogen.

Ethyl acetate gives acetone, carbonic oxide, hydrogen, and ethylene.

Butyric acid gives butyrene, propylene, carbonic oxide, hydrogen, and dimethylbutyrene.

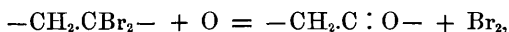
Butyrene gives hydrogen, propylene, and carbonic oxide. From the above, it appears that the action of zinc-dust on both alcohols and acids is essentially a contact action; and in the case of acids may be represented thus:— $2C_nH_{2n+1}.COOH = C_nH_{2n+1}.CO.C_nH_{2n+1} + CO_2 + H_2O$; the carbonic anhydride and water are subsequently reduced by the zinc to carbonic oxide and hydrogen, whilst the hydrocarbons result from the further action of the zinc on the ketone. T. C.

Action of Oxygen on the Bromo-derivatives of Unsaturated Hydrocarbons. By E. DEMOLE (*Bull. Soc. Chim.* [2], **34**, 201—207).—The author has already shown (this Journal, **34**, 401 and 847) that by the action of dry oxygen gas on dibromethylene, it is converted partly into bromacetic bromide and partly into a polymeride. In this reaction, the author was led to suppose that the $C_2H_2Br_2$ split up into C_2HBr and HBr , and that these two bodies united, together with oxygen, to form bromacetic bromide, $C_2HBr + O + HBr = C_2H_2Br_2O$. Finding, however, that by mixing these three gases together, no acid bromide was produced, he arrived at the conclusion that in the first place oxygen was substituted for bromine in $C_2H_2Br_2$, and that then the resulting compound was acted on by the free bromine. This seems probable, since by exposing hydrobromic acid or bromo-compounds to the air, they are gradually decomposed, with liberation of oxygen. By applying this theory to the formation of $POCl_3$ and $POBr_3$ by direct union of PCl_3 or PBr_3 and oxygen gas, it is found that when oxygen gas is passed into boiling phosphorus tribromide, explosions occur from time to time, with liberation of bromine, and the formation of phosphorus oxybromide and phosphorus pentabromide, showing that first a molecule of bromine is liberated with the formation of $POBr$ (?) and that the bromine thus liberated finally unites with PBr_3 and the $POBr$, forming PBr_5 and $POBr_3$.

That a similar reaction takes place in the formation of bromacetic bromide from dibromethylene is seen by passing a slow current of dry oxygen through dibromethylene at the ordinary temperature for 12 hours, washing the gas with water, drying over calcium chloride, and finally passing it into bromine. The product consists chiefly of dibromethylene dibromide (b. p. $190-210^\circ$), produced either according to the equation $C_2H_2Br_2 + Br_2 = C_2H_2Br_4$, or $C_2H_2 + Br_4 = C_2H_2Br_4$, also a solid polymeride of $C_2H_2Br_2$. In the oxidising flask bromacetic bromide, bromacetic acid, and hydrobromic acid were found, and also another polymeride of $C_2H_2Br_2$ (b. p. $220-230^\circ$). The presence of the two last-mentioned acids shows that the oxygen replaces not only bromine, but also hydrogen, the water thus formed decomposing part of the bromacetic bromide. Since the quantity of hydrobromic

acid formed is in excess of that produced by the reaction $\text{C}_2\text{H}_2\text{BrO} \cdot \text{Br} + \text{H}_2\text{O} = \text{C}_2\text{H}_2\text{BrO} \cdot \text{HO} + \text{HBr}$, it is evident that the bromine itself replaces hydrogen.

From this it seems probable that oxygen, like chlorine and bromine, has the power of breaking up the double link in the unsaturated carbon compounds, but that, unlike the halogen, it does not attach itself to the free bonds, but leaves the body unsaturated, which, coming in contact with bromine, forms the saturated compound $\text{C}_2\text{H}_2\text{Br}_4$, whilst also at a higher temperature the oxygen expels the halogen,



and these two bodies unite thus: $-\text{CH}_2 : \text{C} : \text{O} - + \text{Br}_2 = \text{CH}_2\text{Br} \cdot \text{CBr} : \text{O}$.

Another example of the liberation of bromine by oxygen is afforded in the formation of pentabromethane from tribromomethylene by the action of air. Lennox (this Journal, 13, 206) assumed this body to be a polymeride of C_2HBr_5 .

The formation of the body with free bonds is merely an hypothesis, and requires further proof. L. T. O'S.

Preparation of Sodium Ferrocyanide. By S. TANATAR (*Dingl. polyt. J.*, 237, 234).—The author found that by digesting pure cyanide of sodium with freshly prepared ferrous oxide in an alcoholic solution, it was readily and completely transformed into sodium ferrocyanide. Soda, unlike potash, does not possess the property of forming cyanogen when fused with nitrogenous charcoal.

The formation of cyanogen by fusing nitrogenous charcoal with potash is generally explained by the fact that the carbon and nitrogen combine with one another, owing to the presence of free metallic potassium, or the potassium combines in the first place with carbon, forming potassium-acetylene, C_2K_2 , which afterwards absorbs nitrogen in the fusion.

The question whether cyanide of potassium is produced in all cases, or whether its formation does not take place when the conditions necessary for the production of free potassium are absent, was investigated by the author, in connection with the behaviour of the sodium compounds in parallel cases. Nitrogenous charcoal (*carbo animalis ex sanguine*, from Trommsdorff) was fused with potassium and sodium compounds, and various reducing agents. The quantity of the cyanide formed was determined after transformation into ferrocyanide. It was found that the sodium compounds also have the property of forming cyanogen, and often act more strongly than the corresponding potassium compounds. The author concludes that the presence of the free alkali-metal is not the cause of formation of cyanogen, as in cases where these alkali-metals cannot be formed in appreciable quantity, cyanogen was nevertheless produced very largely.

The following table shows the production of cyanide and ferrocyanide of sodium and potassium:—

10 grams animal charcoal gave—

				Ferrocyanide of potassium.
1.	Fused with	25 grams	K_2CO_3	2.15 grams.
2.	„	25 „	carbonate of sodium and potassium.....	1.87 „
3.	„	25 „	KCl and 5 grams K_2CO_3 ..	1.72 „
4.	„	25 „	NaCl and 5 grams K_2CO_3 ..	1.81 „
5.	„	25 „	KCl	0.40 „
6.	„	25 „	KCl and 5 grams $CaCO_3$..	1.20 „
7.	„	25 „	KCl and 5 grams Na_2CO_3 ..	1.60 „
8.	„	25 „	KCl, 5 grams Na_2CO_3 , and 3 grams $CaCO_3$	2.00 „
				Ferrocyanide of sodium.
9.	„	25 grams	Na_2CO_3	0.20 grams.
10.	„	25 „	NaCl	0.20 „
11.	„	25 „	NaCl and 5 grams $CaCO_3$..	1.22 „
12.	„	25 „	NaCl and 5 grams Na_2CO_3 ..	2.17 „
13.	„	25 „	NaCl, 5 grams Na_2CO_3 , and 3 grams $CaCO_3$	2.30 „

10 to 15 per cent. of cast-iron borings were added to the mixture in each experiment.

Without the addition of iron to the alkaline chlorides, only traces of cyanogen were formed.

The difficulty of separating sodium ferrocyanide from the melt by crystallisation considerably influences its preparation on a large scale; should this, however, be surmounted, the manufacture of this substance would probably supersede that of potassium ferrocyanide.

D. B.

An Isomeric Potassium Cyanate. By A. BANNOW (*Ber.*, 13, 2201—2202).—The author has previously (*Ber.*, 4, 253) described a potassium cyanate, which differed from ordinary potassium cyanate in many of its properties, but more especially in the fact that by treatment with silver nitrate it gave the silver-salt of a dicyanamide, AgC_2N_3 . It is now shown that this difference was due to the presence of paracyanogen, and that the two potassium cyanates are otherwise identical.

T. C.

Influence of Isomerism of Glycols on the Formation of their Acetates. By N. MENSCHUTKIN (*Ber.*, 13, 1812—1814).—The initial velocity and limit of etherification of typical glycols by acetic acid of various classes are compared (1 mol. glycol to 2 mols. of acid).

		Initial velocity.	Limit.
Primary glycols ..	{ Ethylene glycol, $CH_2.OH.CH_2(OH).OH$ }	42.93	53.86
	{ Trimethylene glycol, $CH_2(OH).CH_2.CH_2.OH$ }	49.29	60.07

		Initial velocity.	Limit.
Primary, secondary glycol	$\left\{ \begin{array}{l} \text{Propylene glycol,} \\ \text{MeCH(OH).CH}_2\text{.OH} \end{array} \right\}$	36.43	50.83
Secondary glycol...	$\left\{ \begin{array}{l} \text{Pseudobutylene glycol,} \\ \text{MeCH(OH)CH.OH.Me} \end{array} \right\}$	17.79	32.79
Tertiary glycol....	$\left\{ \begin{array}{l} \text{Pinacone,} \\ \text{CMe}_2\text{(OH)CMe}_2\text{.OH} \end{array} \right\}$	2.58	5.85
	$\left\{ \begin{array}{l} \text{Resorcin,} \\ \text{C}_6\text{H}_4\text{(OH)}_2 \end{array} \right\}$	0	7.08

From this table, it is evident that there is an analogous influence of isomerism on the etherification of the monohydric and dihydric alcohols; this is even more evident in the latter than the former.

As the author has shown that tertiary alcohols are decomposed on etherification into an olefine, so these experiments point to a similar decomposition of pinacone. Resorcinol in its initial velocity and limit of etherification resembles not only a tertiary glycol, but also a monohydric phenol.

V. H. V.

Synthesis of Glycerol. By LIEBEN and ZEISEL (*Ber.*, **13**, 2032).—The paper is merely a priority claim with regard to the synthesis of a four-carbon glycerol by Markownikoff, and to a study of the reduction of croton aldehyde to croton alcohol, by Karetnikoff.

V. H. V.

Lead Glycerides and the Quantitative Estimation of Glycerol. By T. MORAWSKI (*J. pr. Chem.* [2], **22**, 401—418).—Monoplumboglyceride, $\text{C}_3\text{H}_6\text{PbO}_3$, is best prepared by dissolving 22 grams of lead acetate in 250 c.c. of water, mixing with 20 grams of glycerol, heating, and then adding 15 grams of potash. On standing for one or two days, the clear filtrate deposits the compound in fine needles. By mixing together basic lead acetate and glycerol, and adding a solution of lead oxide in potassium hydrate, a precipitate is obtained of the formula $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Pb}_3$. A third glyceride is obtained as a gummy mass by adding alcoholic potash solution to a mixture of basic lead acetate and glycerol; it has the composition $\text{C}_{12}\text{H}_{21}\text{Pb}_3\text{O}_{13}$. Addition of ammonia to a hot solution of lead nitrate and glycerol yields hard crusts of the compound $2\text{C}_3\text{H}_5\text{O}_2\text{Pb(O.PbNO}_3\text{).Pb(OH)NO}_3$; the same substance is also obtained on boiling together lead oxide, glycerol, and lead nitrate solution. Experiments on the estimation of glycerol by evaporation of its solutions with a weighed amount of lead oxide gave results which, although promising, show that some sources of error have yet to be eliminated.

A. J. G.

Action of Soda on Glycerol. By A. FERNBACH (*Bull. Soc. Chim.* [2], **34**, 146—147).—Belohoubek obtained propyl glycol by the action of soda on glycerol. On repeating the experiment, the author has obtained only about one-tenth of the yield of glycol stated by Belohoubek, and finds that by secondary reactions methyl, ethyl, normal propyl, and isopropyl alcohols are formed, together with olefines con-

taining hexylene, which unites with hydrochloric acid in the cold, yielding diisopropyl chloride (b. p. 115°).

These results show that by this reaction normal alcohols and the olefines $C_nH_{2n} : C.(C_nH_{2n+1})_2$ are formed. L. T. O'S.

A Six-Carbon Glycerol. By W. MARKOWNIKOFF (*Ber.*, **13**, 1842—1843).—The author has obtained from crotonylmethylcarbinol, $CH_2:CH.CH_2.CH_2.CHMe.OH$ (Wurtz, *Jahresh.*, 1864, 515; Crow, *Annalen*, **201**, 42), a triacetin of a glycerol, $C_6H_{11}(OH)_3$, boiling at 270—280°, and at 192—196° at a pressure of 100 mm. The triacetin is a thick, colourless bitter liquid, insoluble in water; its sp. gr. is 1.087 at 0°. On saponification, the glycerol is obtained as an oily liquid, but owing to the small quantity no analyses were made. By reduction of allylacetone, Rablukoff has obtained, besides crotonylmethylcarbinol, a liquid boiling at 254—262°, which is probably the pinacone of allylacetone, $C_3H_5.CMe(OH).CMe(OH).C_3H_5$.

V. H. V.

Polyhydric Alcohols. By N. MENSCHUTKIN (*Ber.*, **13**, 1814—1816).—The author remarks that the perfect analogy which exists in the etherification of mono- and di-hydric alcohols would lead to the conclusion that in polyhydric alcohols corresponding changes of chemical structure would give rise to corresponding changes of etherification.

I. *Etherification of Polyhydric Alcohols with the equivalent number of molecules of Acetic Acid.*—The following table gives the etherification data of polyhydric alcohols:—

	Atomicity of alcohol. No. of mols. of acetic acid.	Initial velocity.		Limit
		Absolute.	Relative.	
Ethyl alcohol ..	1	46.81	70.31	66.57
Ethylene glycol.	2	42.64	79.58	53.94
Glycerol	3	36.26	78.82	46.00 [45.4]*
Erythrol	4	24.91	62.16	40.07
Mannitol	6	20.56	77.80	26.42

This table shows that as the number of OH groups in the alcohol increases, the initial velocity and limit of etherification decrease, as also the capacity for etherification. The decrease cannot be attributed entirely to an increase of secondary alcoholic groupings, for the same phenomenon is observable in ethyl alcohol and ethylene glycol, both of which contain only primary alcoholic groupings.

II. *Etherification of Polyhydric Alcohols with Acetic Acid in equal numbers of molecules of Alcohol and Acid.*—Berthelot has found that in etherification in equal number of molecules all the polyhydric alcohols had the same degree of etherification (about 70 per cent.), which led him to apply etherification as a means of determining the equivalence of a polyhydric alcohol. The author, however, finds that this is not the case with all polyhydric alcohols.

* The numbers in brackets represent the corresponding determinations of Berthelot.

	Initial velocity.	Limit.
Methyl alcohol	55.59	69.59
Glycol	51.88	69.89 [68.8]
Glycerol.....	51.85	70.08 [69.3]
Erythrol.....	53.60	65.73 [69.5]
Mannitol	—	62.53

Differing from these are the following glycols:—

	Initial velocity.	Limit.
Trimethylene glycol.....	59.53	75.59
Propylene glycol	40.67	58.51

The first set of alcohols form a group distinguished by their equality of etherification, but this is not an invariable characteristic of all polyhydric alcohols. The limits given in the above table also point to a diminution of etherification capacity of polyhydric alcohols, since although they contain more equivalents than monohydric, yet the "effect values" (Wirkungswerth) of polyhydric and monohydric alcohols are equal.

III. *Etherification with excess of Acetic Acid.*—The following table gives a compilation of results:—

	<i>Acetic Acid.</i>			
	2 mols.	3 mols.	4 mols.	6 mols.
Glycol	53.72	43.49	36.80	25.00
Glycerol....	55.54	46.00	39.73	31.12
Erythrol....	56.00	—	40.07	31.24
Mannitol ..	—	—	38.47	26.42

This table shows that the alcohols in this group are identical in their etherification, which proves that *the etherification of polyhydric alcohols with free acid is no estimate of the number of OH groups they contain.*

V. H. V.

Multiples in the Optical Rotary Powers of Carbohydrates.

By T. THOMSEN (*Ber.*, **13**, 2168—2169).—The author has determined the value of $[\alpha]_D$ for the following carbohydrates. The values are referred in all cases to the group $C_6H_{10}O_5$, which is contained in all these compounds, or, what is the same thing, to the amount of carbon.

Dextrose	58.8 = 5×11.8
Cane-sugar.....	70.3 = 6×11.7
Wood-gum (<i>Jour. f. Prakt. Chem.</i> , 19 , 146) in alkaline solution	—84 = 7×12.0
Arabinic acid.....	—93.9 = 8×11.7
Arabinose	121.4 = 10×12.1
Maltose	143.5 = 12×12.0
Starch in alkaline solution	168 = 14×12.0
Dextrin	193 = 16×12.1

The table shows that these values of $[\alpha]_D$ are all simple multiples of a common factor.

T. C.

Sorbin and Sorbite. By C. VINCENT (*Bull. Soc. Chim.* [2], **34**, 218—219).—By allowing the juice of the berries of the mountain ash to ferment for about a year and concentrating the solution, large dark-brown crystals of *sorbin* were obtained. On working as above, but with a larger quantity of substance, large quantities of acicular crystals were obtained, and these on crystallisation from hot alcohol presented all the properties of *sorbite*, giving no colour when boiled with alkalis, as sorbin does. The formation of sorbin in one experiment and sorbite in the other is probably due to the action of a certain ferment which is necessary for the formation of sorbin, and was present in the former but absent in the latter case. This may explain why many chemists have failed to obtain sorbin from mountain ash berries, and hence doubted its formation from that source.

Sorbite is isomeric with mannite and dulcitol, and forms with oxalic acid at 75° sorbite-formamide, with evolution of carbonic anhydride. It is a colourless odourless syrup. L. T. O'S.

Inversion of Raw Sugar by Carbonic Acid and some Properties of Inverted Sugar. By E. O. V. LIPPMANN (*Ber.*, **13**, 1822—1826).—Former experiments on the inversion of sugar by carbonic acid have not given concordant results. The author finds that carbonic acid gas has no effect on raw sugar even after six months, but by acting upon the sugar with a solution of the gas in water in a sealed flask the sugar is entirely inverted. The power of inversion of carbonic acid is increased by raising the temperature, and increasing the pressure; the reaction is complete in three-quarters to one hour at a temperature of 100° in a soda-water bottle.

The determinations of specific rotatory power after perfect inversion have varied according to the different observers, using different methods for inversion from -38° to -44.16° ; the author finds -44.19° after inversion with carbonic acid. On warming, the left-handed rotatory power diminishes, becoming *nil* at a temperature of $87.3-91.7^\circ$. The author has made the following determinations ($c = 17.21$):—

0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.
-27.9	-24.5	-21.4	-18	-15.2	-12.0	-8.5	-5.8	-2.6

These values agree with those calculated from Tuchsmidt's formula, $[\alpha_D]t = -(27.6 - 0.32t)$. The author has not succeeded in confirming Maumené's view, that inverted sugar contains besides glucose and levulose a third modification, "inactose," itself present in two modifications. Maumené's result may probably be explained by supposing that the action of lime gives rise to the formation of a glycosate, $2C_6H_{12}O_6 + 3CuO + 2H_2O$, unstable in presence of light, the existence of which has been demonstrated by the researches of Péligot.

V. H. V.

Presence of Saccharin in Osmosed Sugar. By E. O. V. LIPPMANN (*Ber.*, **13**, 1826—1827).—Sugar refiners have found a crystalline sugar when raw molasses is subjected to osmose. The author has heated these crystals with concentrated nitric acid according to Péligot's process, and has separated crystals which were proved by

their chemical properties and polarisation coefficient $[\alpha]_D = +93.5^\circ$, to be identical with Pélégot's saccharin. V. H. V.

Saccharin and Saccharinic Acid. By C. SCHEIBLER (*Ber.*, **13**, 2212—2217).—Saccharin, the new derivative of the glucoses, recently discovered by Pélégot (*Ber.*, **13**, 196), has not the composition $C_{12}H_{22}O_{11}$, as he supposed, but is the anhydride, $C_6H_{10}O_5$, of a new acid, $C_6H_{12}O_6$, which the author calls saccharinic acid. Saccharin (m. p. $160-161^\circ$) decomposes carbonates when boiled with them, and forms saccharinates, from which, however, the free acid cannot be obtained, since at the moment of its liberation it splits up into water and saccharin. Saccharin is probably a lactone having the constitution $CH_2(OH).CH(OH).CH(OH).CH.CH_2.CO$: on reduction with

hydriodic acid it gives a neutral oil (b. p. $203-204^\circ$ uncorr.) consisting no doubt of saccharone, $Me.C_2H_4.CH.CH_2.CO$.

The saccharinates are all exceedingly soluble. The potassium and ammonium salts are crystalline, whilst those of barium, calcium, and sodium dry up to thick syrups. T. C.

Conversion of Starch into Sugar by the Action of Dilute Sulphuric Acid at High Temperatures. By F. ALLIHN (*J. pr. Chem.*, **22**, 46—97).—About 10 grams of anhydrous starch were used in each experiment, and were acted on for various periods by 50 c.c. of acid containing 0.1, 0.2, 0.5, and 1 per cent. at temperatures of 100° , 108° , and 114° . The following results were obtained:—

(1.) The conversion of starch into sugar by dilute sulphuric acid generally takes place more quickly and perfectly the more concentrated the acid is, the longer the period of the reaction, and the higher the temperature.

(2.) The quantity of starch converted into sugar up to 40 to 50 per cent. is proportional to the duration of the reaction.

(3.) In the later stages the reaction becomes gradually slower, so that a perfect conversion, if possible, under the given proportions, can only be reached by an disproportionally long duration of the reaction.

(4.) The reason of the slowness of the reaction is due chiefly to the varying capacity of resistance of dextrin to dilute acids.

G. T. A.

Specific Identity of Inulins and of Natural Levulins. By LEFRANC (*J. Pharm.* [5], **2**, 216—220).—The author establishes the identity of inulins from all sources, on the ground that they all have the same rotatory power $[\alpha]_D = -40$; and, for the same reason, concludes that all natural levulins are identical, their rotatory power $[\alpha]_D = -26$. The levulin obtained by heating inulin with water at 100° the author names *pseudo-levulin*, $[\alpha]_D = -46$.

Preparation of Natural Levulin.—The juice of the artichoke is treated with lead acetate, and the filtered solution freed from lead by means of sulphuretted hydrogen, is finally neutralised with magnesium carbonate. After filtering, the solution is evaporated to a syrupy con-

sistence, and, when cold, the levulin is precipitated with alcohol. The precipitated levulin is dissolved in hot alcohol, treated with animal charcoal, and the solution left to crystallise. The last traces of levulin are precipitated from the mother-liquors by ether. L. T. O'S.

Specific Rotatory Power of Lactose. By E. MEISSL (*J. pr. Chem.*, **22**, 97—103).—The lactose used in the experiments was prepared by acting on milk-sugar with dilute sulphuric acid and crystallising the product from alcohol.

The following tables embody the results obtained with a Wild's polaristrobometer. (p = grams of the substance, q = grams of water) :—

No.	p .	$p + q$.	Sp. gr. at 17·5°.	α at			
				10°.	17·5°.	20°.	30°.
1	2·3702	48·4282	1·01964	8·18	8·02	7·97	7·78
2	4·8989	49·4040	1·04019	17·02	16·69	16·57	16·12
3	9·7367	51·2847	1·07979	34·12	33·46	33·23	32·37
*4	9·6914	51·2465	1·07899	33·91	33·31	33·12	32·28
5	19·4263	54·9350	1·15664	69·17	67·78	67·39	65·72

No.	Weight per cent. P.	$[\alpha]_D$ at							
		10°.		17·5°.		20°.		30°.	
		Found.	Cal.	Found.	Cal.	Found.	Cal.	Found.	Cal.
1	4·89	82·06	82·18	80·45	80·61	79·95	80·09	78·05	78·00
2	9·92	82·58	82·57	80·97	81·00	81·39	80·48	78·21	78·39
3	18·98	83·32	83·28	81·71	81·72	81·15	81·19	79·05	79·10
4	18·91	83·20	83·28	81·72	81·72	81·26	81·19	79·20	79·10
5	35·36	84·66	84·57	82·96	83·00	82·50	82·48	80·44	80·39

To find the weight per cent. P of lactose in a solution which rotates α° , the formula $\frac{100\alpha}{L.d. \cdot [\alpha]}$ may be used. If the value for $[\alpha]_D$ at t° in P per cent. solution be introduced into this formula we obtain—

$$P = \frac{100 \alpha}{L.d. (83,883 + 0.0785 P - 0.209 t)}$$

If $83,883 - 0.209 t = A$, and $0.0785 = B$, we get—

$$P = \sqrt{\left(\frac{A}{2B}\right)^2 + \frac{100\alpha}{B.L.d} - \frac{A^1}{2B}}$$

G. T. A.

* Recrystallised three times from methyl alcohol.

Anhydrous Milk-sugar. By E. O. ERDMANN (*Ber.*, **13**, 2180—2184).—Milk-sugar can exist in the anhydrous state in three different modifications, two of them solid and crystalline, and the third liquid.

(a.) This is obtained when an ordinary solution of milk-sugar is quickly boiled in a metal vessel; the solution after a certain time suddenly solidifies to a porous mass consisting of small anhydrous crystals. These have a low rotatory power which gradually increases, and are very soluble in water.

(b.) This solid modification is obtained by dehydrating ordinary milk-sugar at 130°. It has a high rotatory power, which gradually diminishes on keeping until it is identical with that of the form (a). It is much less soluble in water than the form (a).

(c.) An unstable liquid modification, obtained by the gradual transformation of the solutions of the two preceding forms on keeping. It is stable only in the dissolved state, for on crystallisation it changes in the presence of water into ordinary hydrated milk-sugar, whilst on driving off the water by boiling, it gives the anhydrous form (a).

T. C.

A Hitherto Unobserved Property of Milk-sugar. By M. SCHMOEGER (*Ber.*, **13**, 1915—1931).—The author has found that milk-sugar not only exhibits bi-rotation (the high rotatory power of a freshly-prepared solution of the crystallised sugar) and normal rotation (the rotatory power of the same solution after standing), but that under certain circumstances it exhibits a third rotation, lower than either of the others, to which he applies the term *semi-rotation* ("Halb-rotation"). Crystallised milk-sugar, $C_{12}H_{22}O_{11} + H_2O$, dried in the air or over sulphuric acid, does not lose weight at 100°; but when a solution of the crystals is evaporated to dryness over boiling water the residue is anhydrous. A solution of this residue in cold water exhibits in the polariscope at first semi-rotation, changing in the course of a few hours to normal rotation. The normal specific rotatory power of crystallised milk-sugar at 20° is $[\alpha]_D = 52.53^\circ$. The ratio of semi-rotation to normal rotation is 5 : 8 (about); and the ratio of normal to bi-rotation is also 5 : 8. Anhydrous milk-sugar, obtained by evaporating its solution at 100°, when dissolved in hot water, exhibits normal and not semi-rotation. A solution in cold water of the anhydride obtained by heating the crystallised sugar to 130°, exhibits bi-rotation.

J. R.

NOTE.—In *Ber.*, **13**, 2130—32, the question of priority between the author and Erdmann is discussed.

Isopropylene-neurine. By H. T. MORLEY (*Ber.*, **13**, 1805—1806).—On heating on a water-bath a mixture of isopropylene chlorhydrin and trimethylamine, a crystalline mass of trimethylhydroxyisopropylammonium or propylene-neurine chloride, $CH_2(OH).CHMe.NMe_3Cl$, is obtained; it forms colourless, transparent, deliquescent crystals, which turn brown in the presence of air. The platinochloride forms feathery leaflets.

V. H. V.

Dimethylhydrazine. By E. RENOUF (*Ber.*, **13**, 2169—2174).—This is a more complete investigation of the dimethylhydrazine first

obtained by E. Fischer (*Ber.*, **8**, 1587), by the reduction of the nitroso-compound of dimethylamine.

Dimethylnitrosamine, NMe_2NO , is a yellow alkaline oil (b. p. 148.5° at 724 mm.), having great resemblance to the corresponding diethyl-compound. It forms the hydrochloride $\text{NMe}_2(\text{NO})\text{HCl}$, and on boiling with hydrochloric acid splits up into dimethylamine and nitrous acid.

Dimethylhydrazine, NMe_2NH_2 , is obtained as a colourless oil (b. p. 62.5° at 717 mm.) by the reduction of the preceding compound. It is very hygroscopic, and is easily soluble in water, alcohol, and ether. Its sp. gr at 11° is = 0.801. It forms two series of salts with acids. The acid hydrochloride, $\text{NMe}_2\text{NH}_2 \cdot 2\text{HCl}$, is obtained in crystals by passing an excess of hydrochloric acid into the alcoholic solution of the base; by long-continued heating at 105° it is converted into the neutral salt $\text{NMe}_2\text{NH}_2\text{HCl}$. The platinochloride, $(\text{NMe}_2\text{NH}_2\text{HCl})_2\text{PtCl}_4$, the neutral sulphate, $(\text{NMe}_2\text{NH}_2)_2\text{H}_2\text{SO}_4$ (m. p. 105°), and the acid oxalate, $\text{NMe}_2\text{NH}_2 \cdot \text{C}_2\text{O}_4\text{H}_2$, are also described.

Dimethylhydrazine is decomposed by nitrous acid into dimethylamine, nitrous oxide, and water. It combines directly with carbon bisulphide to form the hydrazine salt of dimethylsulphocarbazineic acid, $\text{NMe}_2\text{NH} \cdot \text{CS} \cdot \text{S} \cdot \text{N}_2\text{H}_3\text{Me}_2$, which is easily soluble in water, and decomposes on heating; on adding acetic acid to its concentrated aqueous solution, it gives the free *dimethylsulphocarbazineic acid*, $\text{NMe}_2\text{NH} \cdot \text{CS}_2\text{H}$, which crystallises in colourless leaflets (m. p. 112°).

Dimethylhydrazine combines directly also with phenyl isocyanate to form a carbamide, having the composition $\text{CO}(\text{NHPh}) \cdot \text{NH} \cdot \text{NMe}_2$. It crystallises in double pyramids (m. p. 108°), and when boiled with hydrochloric acid splits up into dimethylhydrazine and phenylisocyanate.

On warming dimethylhydrazine with an alcoholic solution of ethyl oxalate, the oxamide, $\text{CO}(\text{NH} \cdot \text{NMe}_2)_2$, is obtained in white leaflets (m. p. 220°), easily soluble in water and alcohol; ethyl chloride, bromide, and iodide all act violently on dimethylhydrazine, the chief product being the corresponding azonium-compound. Dimethylethylazonium chloride is a very soluble crystalline substance which forms a crystalline platinochloride, $(\text{NMe}_2\text{EtCl} \cdot \text{NH}_2)_2\text{PtCl}_4$. On reduction with zinc-dust and acetic acid, it is decomposed into dimethylethylamine, ammonia, and hydrochloric acid. Dimethylhydrazine, like primary hydrazines, combines with potassium pyrosulphate to form potassium dimethylhydrazinesulphonate, $\text{NMe}_2\text{NH} \cdot \text{SO}_3\text{K}$.

Tetramethyltetrazone, N_4Me_4 , is obtained by oxidising an ethereal solution of dimethylhydrazine with mercuric oxide. It is a pale-yellow oil, which is but little soluble in water, and distils undecomposed at about 130° , but if heated slightly above this point it explodes with great violence. It is a strong base with alkaline reaction. Its salts are mostly soluble in water and in alkalis; of these the picrate, $\text{Me}_2\text{N}_4\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, is the most characteristic, and crystallises in yellow prisms which are sparingly soluble in alcohol, but easily soluble in water. Tetrazone reduces silver nitrate, and on boiling with dilute acids it gives dimethylamine, monomethylamine, formic aldehyde, and nitrogen.

T. C.

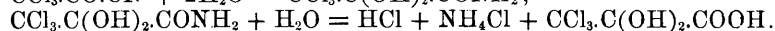
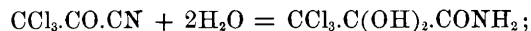
Decomposition of Copper Acetate in presence of Water. By P. CAZENEUVE (*J. Pharm.* [5], 1, 409—412).—The author has already shown (this Journal, 38, 32) that acetic acid is oxidised by cupric oxide to glycollic acid with formation of cuprous oxide; at the same time, small quantities of propionic acid are formed, with liberation of carbonic anhydride, due to a secondary reaction. This, however, is not strictly the case, since by substituting basic cupric acetate for the neutral salt, the quantity of carbonic anhydride evolved increases considerably without a corresponding increase in the quantity of propionic acid. Its formation is therefore due to the complete combustion of the acetic acid.

Ordinary verdigris heated with water under pressure at 200° for from 1 to 24 hours, showed that first the neutral acetate is formed with separation of cupric oxide, and, as the heating is continued, carbonic anhydride is evolved, and the cupric acetate gradually lessens in quantity; finally the cupric is converted into cuprous oxide, and large quantities of calcium glycollate (lime being contained in the verdigris as impurity) and free glycollic acid are formed. The proportion of glycollic acid obtained from basic cupric acetate is much less than is obtained from the neutral salt.

The cuprous oxide is obtained in cubical and octohedral crystals.

L. T. O'S.

Some Derivatives of Trichloroacetyl Cyanide (Synthesis of Isotrichloroglyceric Acid). By L. CLAISEN and P. J. ANTWEILER (*Ber.*, 13, 1935—1940).—Hofferichter's statement (*J. pr. Chem.* 20, 195; this Journal, 1880, Abstr., 35) that when trichloroacetyl cyanide is treated with hydrochloric acid it yields a body of the formula $C_3HCl_3O_3$ is found by the authors to be incorrect. The ultimate product of this action is Strecker's isotrichloroglyceric acid, but by very careful treatment of the cyanide with hydrochloric acid the amide of the acid is formed as an intermediate product. The entire reaction is expressed by the equations:—



Trichloroacetyl Cyanide, $CCl_3.CO.CN$.—Hofferichter obtained this substance by the action of silver cyanide on trichloroacetic bromide, but it is more easily and cheaply prepared by boiling together equivalent quantities of mercuric cyanide and trichloroacetic bromide. The pure cyanide boils at 121—122°.

The amide of isotrichloroglyceric acid, $CCl_3.C(OH)_2.CO.NH_2$, is readily obtained by adding 1 mol. of the cooled cyanide to 2 mols. of water saturated with hydrochloric acid at 0°. In the course of 12 hours, the whole solidifies to a mass of crystals of the amide mixed with some trichloroacetic acid.

The pure amide forms a white crystalline mass melting at 126—127°. When heated, even below its melting point, it gradually gives off 1 mol. of water and is converted into a white body, $CCl_3O_2H_2N$, the constitution of which is as yet uncertain.

Isotrichloroglyceric acid, $CCl_3.C(OH)_2.COOH$, is best obtained by heating the foregoing amide with hydrochloric acid in sealed tubes.

It crystallises in short, colourless, non-deliquescent prisms, melting at 102° , and is soluble in all proportions of water. It reduces Fehling's solution and ammoniacal silver nitrate. The *barium salt* forms small prismatic crystals, soluble in water. When heated with potash or soda, and to some extent even when neutralised with alkaline carbonates in the cold, the acid splits up into chloroform and oxalates.

J. R.

Formation of α - and β -Chlorolactic Acids. By P. MELIKOFF (*Ber.*, 13, 2153—2155).—The product obtained by the action of hypochlorous acid on acrylic acid does not consist of α -chlorolactic acid only, as previously stated (*Ber.*, 13, 956), but is a mixture of α - and β -chlorolactic acids. These acids are easily separated by means of the zinc salts, that of the β -acid being insoluble in alcohol, whilst the other is very soluble.

α -Chlorolactic acid, $C_3H_5ClO_3$, could only be obtained as a thick syrup. On reduction with hydriodic acid, it gives β -iodopropionic acid (m. p. 82°). Its zinc salt is a non-crystalline hygroscopic gummy mass, easily soluble in alcohol and in water.

β -Chlorolactic acid, $C_3H_5ClO_3$, crystallises in prismatic needles (m. p. 78°) or tables. Its zinc salt is insoluble in alcohol, and has the composition $(C_3H_4ClO_3)_2Zn + 3H_2O$. The acid is identical with the β -chlorolactic acid obtained by the action of hydrochloric acid on glycidic acid.

T. C.

Propionyl-formic Acid. By L. CLAISEN and E. MORITZ (*Ber.*, 13, 2121—2123).—*Propionyl cyanide*, $C_3H_5O.CN$, is formed, together with other products, by heating propionic chloride with silver cyanide at 100° . It is a colourless liquid (b. p. 108 — 110°), which becomes yellow on keeping, and is decomposed by water into hydrocyanic and propionic acids.

Dipropionyl dicyanide $(C_3H_5O.CN)_2$, is formed together with the preceding compound as a colourless, syrupy liquid (b. p. 210 — 213° , lighter than water. It has a peculiar smell, resembling that of ethyl benzoate.

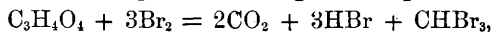
Propionyl formamide, $C_3H_5O.CO.NH_2$, is obtained by the action of fuming hydrochloric acid on the cyanide. It crystallises in prisms and leaflets (m. p. 116 — 117°), which are easily soluble in water and in alcohol, but less so in ether.

Propionyl-formic acid, $C_3H_5O.COOH$, is formed by the action of the most concentrated hydrochloric acid on the well-cooled cyanide. It is a colourless and somewhat syrupy liquid, which is miscible with water, alcohol, and ether. It has a peculiar and persistent smell of pyrotartaric acid. It boils without decomposition at 74 — 78° under a pressure of 25 mm. Sp. gr. at $17.5 = 1.20$. The *silver salt* crystallises in concentric or feathery groups of needles, which are only moderately soluble in cold but easily in hot water, and are decomposed on boiling with precipitation of metallic silver. The *barium salt* crystallises in small flat prisms or leaflets with 1 mol. of water. It is much less soluble in water than barium propionate.

Propionyl-formic acid gives α -oxybutyric acid (m. p. 42 — 43°) when reduced with sodium amalgam.

T. C.

Action of Bromine on Malonic Acid. By E. BOURGOIN (*Bull. Soc. Chim.* [2], **34**, 215—218).—When 5 grams malonic acid, 10 c.c. bromine, and 12 c.c. water are mixed together, the temperature rises to 50—60°, and a little carbonic anhydride is evolved. The mixture is then heated at 120° under pressure for 18 hours, and finally at 145°, when two layers of liquid are formed. The upper layer consists of an aqueous solution of tribromoacetic acid, whilst the lower layer is bromoform. Large quantities of carbonic anhydride and hydrobromic acid are formed in the reaction. The explanation of the formation of bromoform has not yet been established, but it appears probable that some unstable bromo-acids are produced, which, under the conditions of experiment, are decomposed according to the equation :—



a reaction analogous to that by which bromethylene bromide is obtained from succinic acid. L. T. O'S.

Action of Water on Ethyl Malonate at a High Temperature. By E. HJELT (*Ber.*, **12**, 1949).—The author finds by direct experiment that ethyl malonate, when heated with five times its weight of water in a sealed tube, is resolved at about 150° into ethyl acetate and carbonic anhydride. A quantity of free acetic acid is also produced by the further reaction of the ethyl acetate with water at the temperature of the experiment. J. R.

Itaconic Anhydride. By W. MARKOWNIKOFF (*Ber.*, **13**, 1844—1848).—The author has studied the action of acetic chloride on silver itaconate in ethereal solution, and obtained after purification a substance which crystallises in clear transparent rhombic prisms (m. p. 68·5°), whose aqueous solution gives itaconic acid. The anhydride distills at 210° (citraconic anhydride 212°). Anschütz and Petri had studied the action of acetic chloride on itaconic acid, but without any decided result. The author is endeavouring to prepare anhydrides of isoterephthalic and terephthalic acids. V. H. V.

Behaviour of Glyoxylic Acid with Potash. By C. BÖTTINGER (*Ber.*, **13**, 1931).—Glyoxylic acid, when heated with potash solution, yields oxalic and glycollic acids, but no acetic acid. This fact is used by the author in support of his theory of the formation of uvitic acid from pyroracemic acid. J. R.

Formation of Uvic (Pyrotritaric) Acid. By C. BÖTTINGER (*Ber.*, **13**, 1969).—This acid is obtained in large quantity on heating a mixture of pyroracemic acid with an equal weight of dry sodium acetate and twice its weight of acetic anhydride at 140° for 3 hours. The product of the reaction is dissolved in water, and boiled with soda until an oil which floats on the surface disappears, whereupon the liquid is acidified with sulphuric acid. The yield is 20 per cent. or more of the pyroracemic acid taken. J. R.

Synthesis of Tri- and Tetra-basic Fatty Acids. By C. A. BISCHOFF (*Ber.*, **13**, 2161—2165).—The author applies Conrad's (*Ber.*,

12, 752) method of preparing polybasic acids by the use of ethyl malonate to the synthesis of a number of acids.

Ethenyltricarboxylic Acid, $C_2H_3(COOH)_3$, obtained by the saponification of the ethyl salt (Full, *Ber.*, **12**, 752) crystallises in colourless prisms, which are soluble in alcohol, ether, and water. It forms well-crystallised salts, and its aqueous solution decomposes carbonates and precipitates the lead from a solution of lead acetate. It melts at 158° , with evolution of carbonic anhydride and formation of succinic acid. It is identical with the acid which Conrad and the author obtained (*Ber.*, **13**, 601) by the saponification of ethyl acetylenetetracarbonate (compare also Orlowsky, *Ber.*, **11**, 1604).

Monochlorethenyltricarboxylic Acid, $C_2H_2Cl(COOH)_3$.—The ethyl salt of this acid is obtained, by the action of chlorine gas on ethyl ethenyltricarboxylate, as a colourless liquid (b. p. 290° with partial decomposition). On boiling with aqueous hydrochloric acid, it gives fumaric and carbonic acids, and on saponification with potash, yields inactive malic acid identical with that obtained by Lloyd (*Ann. Chem. Pharm.*, **192**, 80) from fumaric acid.

Isosallylenetetracarboxylic Acid, $C(COOH)_2(CH_2.COOH)_2$.—The ethyl salt of this acid is obtained by the successive action of sodium ethylate and ethyl monochloracetate on ethyl ethenyltricarboxylate. It is a colourless oil (b. p. 199 – 201° at 25 mm. without decomposition; b. p. 293 – 296° at 725 mm. with slight decomposition). The free acid crystallises in prisms which are soluble in water, ether, and alcohol, and forms well-crystallised salts. It melts at 151° , with evolution of carbonic anhydride, and formation of tricarballic acid.

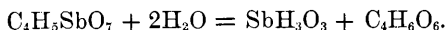
Propenyltricarboxylic Acid $(COOH)_2CH.CHMe(COOH)$.—The ethyl salt of this acid is obtained by the action of ethyl α -bromopropionate on ethyl sodium malonate. It is a colourless oil (b. p. 178 – 180° at 25 mm. without decomposition, and under ordinary pressure at about 270° with slight decomposition). The free acid has not yet been isolated. T. C.

Tanatar's Dihydroxyfumaric Acid. By A. KEKULÉ and R. ANSCHÜTZ (*Ber.*, **13**, 2150–2152).—The dioxifumaric acid, $C_4H_4O_6$, obtained by Tanatar (*Ber.*, **12**, 2293; **13**, 159) from the oxidation of fumaric acid with potassium permanganate, is not a dihydroxyfumaric acid, but is identical with ordinary tartaric acid. T. C.

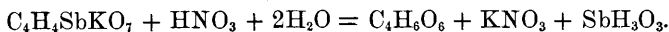
Constitution of Tartar Emetic. By F. W. CLARKE and HELENA STALLO (*Ber.*, **13**, 1787–1796).—The hitherto received hypothesis of the constitution of tartar emetic is that it contains a monatomic radical, SbO , acting as a base; this the authors consider superfluous, and they regard it as the potassium salt of a new acid. Their experiments are grounded on the decomposition of the double barium antimony tartrate with sulphuric acid. On filtering off the barium sulphate formed the clear solution becomes turbid, a white precipitate separating out. This separation depends on the temperature and degree of dilution. On evaporating the turbid solution, a hard white substance is left which is easily soluble in water, and can be recovered from its solution.

According to the authors' view this solution contains an acid which is tartar emetic with the potassium atom replaced by hydrogen, a body of the empirical formula, $C_4H_5SbO_7$. On account of the instability of this acid, indirect methods of analysis were used; its solution was neutralised with the carbonates of potassium, barium, zinc, cobalt, and strontium. With potassium carbonate, the acid gave tartar emetic; with barium, cobalt and zinc carbonates, the double antimony salts of these metals; with strontium carbonate, a salt whose atom relations of the metals were in the ratio $Sr_4 : Sb$, not $Sr : Sb_2$. It was found on decomposing barium antimony tartrate with sulphuric acid, that practically all the antimony was in the filtrate. This fact, together with the regeneration of the barium and potassium salts from the acid, points to the existence of the compound $C_4H_5SbO_7$. Péligot has described an acid antimony tartrate of formula $C_4H_3SbO_6$, which could be represented as $(C_4H_5SbO_7 - H_2O)$, but on preparing this salt by Péligot's method it was found that its solution and that of the authors' acid were not identical. It is probable that there exist two isomeric compounds of the formula $C_4H_5SbO_7$.

On examining the white precipitate formed in the decomposition of the unstable acid, it was found to be orthoantimonious acid—



It is well known that concentrated acids and alkalis thrown down, a white precipitate from tartar emetic solutions; this is not a "basic compound" as hitherto supposed, but orthoantimonious acid—



In fact, the nitric acid combines with the potassium, setting the acid $C_4H_5SbO_7$ free; this is immediately decomposed, with formation of orthoantimonious acid. According to this hypothesis, the result is explained that, on decomposition of tartar emetic with acid, only a part of the antimony is precipitated. The authors express the constitution of their antimony acid and tartar emetic by the formulæ $Sb'''C_4H_4O_6''$ and $Sb'''C_4H_4O_6''$, the neutral tartrate described by Berze-

lius as $Sb_2O \begin{smallmatrix} C_4H_4O_6 \\ O \end{smallmatrix}$, Péligot's compound as $Sb \begin{smallmatrix} C_4H_5O_6 \\ OH \end{smallmatrix}$, and Knapp's

acid tartar-emetic as $Sb \begin{smallmatrix} C_4H_5O_6 \\ OK \end{smallmatrix}$. In none of these compounds is it

necessary to suppose the presence of a group SbO .

V. H. V.

Ferrous Sucrocarbonate. By C. TANRET (*J. Pharm.* [5], 2, 469—471).—By substituting cane-sugar for milk-sugar in the preparation of "*masse de vallet*," a syrupy mass interspersed with crystals is obtained. The crystals are of a brown colour and opaque; the angle between the lateral faces is 79.40° . Sp. gr. = 1.85. They are decomposed by the neutral solvents of sugar, the sugar going into solution and ferrous carbonate being precipitated. The sugar acts but feebly on Fehling's solution until heated with acid, when it readily reduces

it. The analysis of the crystals corresponds with the formula $(C_{12}H_{22}O_{11})_3(Fe_2CO_3)_2$. L. T. O'S.

On Cholic Acid containing Solid Fatty Acids. By P. LATSCHINOFF (*Ber.*, 13, 1911—1915).—The author has previously shown that cholic acid cannot be freed from admixed stearic and palmitic acids by treatment with ether or alcohol. The present paper gives the results of further experiments on the subject. When a mixture of 4 parts of cholic acid and 1 part of stearic acid (mixed stearic and palmitic acids melting at 58°) is dissolved in aqueous ammonia, and the filtered liquid is acidified with hydrochloric acid, the precipitate of cholic and stearic acids thereby thrown down is perfectly tasteless, whereas pure cholic acid is distinctly bitter. The dried precipitate is not affected, or is only partially melted at 135 — 140° , and the stearic acid in it shows little sign of volatility at 140° , although pure stearic acid is freely volatile at that temperature.

On cooling a hot alcoholic solution containing cholic and stearic acids in the above proportion, well formed homogeneous prismatic crystals are deposited, with only here and there a trace of laminæ; and after washing thoroughly with ether, the crystals remain perfectly homogeneous, although they contain a considerable proportion of stearic acid.

Equally peculiar is the behaviour of the barium salt of the mixed acids. Barium cholate is easily and completely decomposed by solution of ammonium carbonate, whereas barium stearate is scarcely affected by it. But when the barium salt of the two acids mixed in the above proportion (4 : 1) is digested for 12 hours with a solution of ammonium carbonate, nearly the whole (95 per cent.) of the stearic acid goes into solution.

The foregoing facts appear to point to a kind of combination of cholic and stearic acids. The combination, however, is of an indefinite and feeble character, for when mixtures of the two acids are treated with ether or carbon bisulphide, the solutions formed contain a very much larger proportion of stearic acid than the undissolved residues.

When more than 20 per cent of stearic acid is present in the mixture, its properties are less completely masked. Taurocholic acid modifies the properties of fatty acids in a still more marked manner, appearing to form with them compounds easily soluble in water.

J. R.

Ethylphosphordichloride and its Homologues. By A. MICHAELIS (*Ber.*, 13, 2174—2176).—*Ethylphosphordichloride*, PCl_2Et , is obtained by heating a mixture of mercuric ethide and phosphorus trichloride (1 : 4) in sealed tubes at 230° . It fumes in the air, and has a peculiar odour, resembling that of apples; it is decomposed by water, and the solution, when evaporated with strong hydrochloric acid, gives Hofmann's ethylphosphinic acid, $EtPO_3H_2$.

Ethylphosphortetrachloride, PCl_4Et , is formed, together with a chlorinated ethane, by the direct combination of chlorine with the preceding compound. It does not melt when heated in an open tube, but in a closed tube it melts slowly, with decomposition at 100° , and quickly

at 160°, forming phosphorus trichloride, ethylphosphordichloride, ethyl chloride, and free chlorine.

Ethylphosphoroxychloride, PEtCl_2O , is a liquid, boiling at about 175°, and is rapidly decomposed by water. It is isomeric with Menschutkin's oxethylphosphorchloride, PCl_2OEt (b. p. 117°).

Isopropylphosphordichloride, PCl_2Pr , obtained in a manner similar to the ethyl compound from mercuric isopropide and phosphorus trichloride, is a liquid (b. p. 135°).

The above facts show that mercuric alkyls behave differently to the zinc alkyls as regards their action on inorganic chlorides, for whereas the latter replace *all* the chlorine atoms of the inorganic chloride, the former replace them in stages. T. C.

Formula of Benzene. By J. THOMSEN (*Ber.*, **13**, 2166—2168).—This is a discussion of the contradictory conclusions arrived at by Bruhl and by the author, as to the constitution of benzene. The former, from his investigation of the molecular refraction of bodies, considers that benzene contains three double linkings, whereas the latter, from his determination of the heat of combustion of benzene (this vol., p. 135) concludes that it does not contain any double linkings, but nine single linkings. T. C.

Nature of Caucasian Petroleum. By F. BEILSTEIN and A. KURBATOW (*Ber.*, **13**, 1818—1821).—It is known that hydrocarbons obtained from Caucasian petroleum by fractional distillation have a higher specific gravity than those of the same boiling point from American petroleum.

	Caucasian petroleum.	American petroleum.
B. p.	Sp. gr.	Sp. gr.
80°	0.717	0.669 (hexane)
95—100°	0.748	0.699 (heptane)

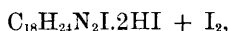
The Caucasian petroleum has also a 10 per cent. higher lighting power than the American oil. The authors have examined specimens of the Caucasian oil, and even after nine distillations could not obtain products of constant boiling points, nor were they able to extract any aromatic hydrocarbon on treatment with fuming nitric acid, nor any olefine by bromine. It appears that the hydrocarbons of Caucasian petroleum are *identical with the additive hydrogen-products of the aromatic hydrocarbons* described by Wreden (*Annalen*, **187**, 166). As a confirmation of the view, the authors obtained trinitroisoxylene from the portion boiling at 115—120°, and from the portion boiling at 95—100°, an oil, hexahydrotoluene, C_7H_{14} , unacted upon by nitric acid. From the portion boiling at 210—215°, a nitro-compound, $\text{C}_6\text{H}_{11}\text{NO}_2$, was prepared, which was not fully investigated. V. H. V.

Hydrocarbons from American Petroleum. By F. BEILSTEIN and A. KURBATOW (*Ber.*, **13**, 2028—2029).—The authors have established the presence of hydrocarbons of the C_nH_{2n} series in petroleum from the Caucasus, and by the action of nitric acid the probable absence of hydrocarbons of the $\text{C}_n\text{H}_{2n+2}$ series. These results are con-

firmed by experiments, which show that crude heptane obtained by fractional distillation is converted into pure heptane by the action of nitric acid. As the crude heptane has a higher specific gravity (·7192) than the purified product (·6927), and contains less hydrogen than that required by theory, and is attacked by nitric acid, it appears that American petroleum, like petroleum from the Caucasus, contains addition-products of the aromatic hydrocarbons. By the action of nitrosulphuric acid on American petroleum, a small quantity of trinitroisoxylene was formed. Further, by the treatment of the crude petroleum with nitric acid, besides pure heptane, a nitrogen compound of formula $C_7H_{15}NO_2$ was obtained, the Caucasian petroleum yielding under the same circumstances a compound of the formula $C_6H_{11}NO_2$.

V. H. V.

Action of Dimethylaniline on Ethylene Bromide and Acetylene Tetrabromide. By P. SCHOOP (*Ber.*, 13, 2196—2200).—*Tetramethyldiamidodiphenylethane*, $NMe_2.C_6H_4.CH_2.CH_2.C_6H_4.NMe_2$, is obtained by warming ethylene dibromide for several days with dimethylaniline. It crystallises in fine silky needles (m. p. 50° , b. p. over 300°), which are easily soluble in ether, light petroleum, and hot methyl or ethyl alcohol, but insoluble in water. It forms well characterised salts, which are decomposed at 100° . The hydrochloride and hydrobromide are very soluble in all solvents except benzene, whilst the hydriodide is much less soluble. The compound



is obtained by acting on the base with hydriodic acid containing free iodine.

The *platinochloride*, $C_{18}H_{24}N_2I \cdot 2HCl.PtCl_4$, is sparingly soluble in water and alcohol, and is decomposed at 100° .

The *oxalate*, $C_{18}H_{24}N_2 \cdot 2C_2O_4H_2$, is crystalline, and is decomposed into free base and acid when heated with water at 80° .

The *picrate*, $C_{18}H_{24}N_2 \cdot 2C_6H_2(NO_2)_3.OH$, is a bright yellow precipitate, which is easily soluble in hot methyl or ethyl alcohol, but only sparingly in ether, chloroform, and light petroleum. The free base on oxidation gives quinone and aldehyde.

Octomethyltetramidotetraphenylethane,



is obtained by the action of dimethylaniline on acetylene tetrabromide. It separates from alcohol in columnar crystals (m. p. 90° , b. p. 300°), which are easily soluble in alcohol, ether, wood spirit, and benzene; less soluble in light petroleum, and insoluble in water.

The *platinochloride*, $C_{34}H_{42}N_4 \cdot 4HCl \cdot 2PtCl_4$, is a bright yellow, amorphous precipitate, which is decomposed on drying at 100° .

The *picrate*, $C_{34}H_{42}N_4 \cdot C_6H_2(NO_2)_3.OH$, forms brilliant yellow scales, readily soluble in hot water and alcohol, but only sparingly in ether. The free base on oxidation with ferric chloride, &c., gives quinone.

Both the ethylene and acetylene bases give by cautious oxidation brilliant dye-stuffs, which are under investigation.

T. C.

Action of Nitrosodimethylaniline Hydrochloride on the Phenolsulphonic Acids which do not contain the Methyl-group. By J. H. STEBBINS (*Ber.*, **13**, 2178—2179).—The author extends Meldola's (*ibid.*, **12**, 2065) action of nitrosodimethylaniline hydrochloride on phenols to phenolsulphonic acids. 1 molecule of sodium β -naphtholsulphonate, dissolved in an equal quantity of glacial acetic acid at 110° , unites directly with 1 molecule of nitrosodimethylaniline hydrochloride to form a beautiful blue dyestuff. The pure substance is a bronze-coloured powder, which is easily soluble in water, and after acidifying dyes silk and wool a fine blue. It has both acid and basic properties, forming colourless compounds with bases, and blue with acids. T. C.

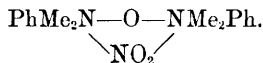
Condensation of Tertiary Bases by Nitric Oxide. By E. LIPPMANN and R. LANGE (*Ber.*, **13**, 2136—2141).—Nitric oxide resembles nitrous acid in its action on primary bases, but behaves very differently towards tertiary bases, for whereas nitroso-compounds are produced by the action of nitrous acid, nitric oxide forms condensation-products.

Dimethylaniline when subjected to the action of nitric oxide in the cold becomes green after four or five days, and large quantities of carbonic anhydride are evolved; after from six to ten days' action it becomes red, and subsequently deposits bright red needles (A), amounting to 5—10 per cent. of the base used. After a continued action for three or four weeks, a violet dyestuff (B) and a body consisting of brilliant white leaflets (C) are obtained.

The bright red needles (m. p. 26.6°) have the composition $C_9H_{13}N_2$, and probably the constitution $PhMe_2N:N:CH$, or possibly $PhN:CH.NMe_2$. It is insoluble in water, sparingly soluble in ether and in alcohol, but very soluble in boiling benzene. It dissolves in glacial acetic acid with an intense green colour, and is reprecipitated therefrom unchanged on the addition of water. The purple hydrochloride as well as the other salts are somewhat unstable compounds. Platinum chloride and mercuric chloride give carmine-red precipitates.

The white leaflets (C) consist of *tetramethyldiphenyldiamine*, $PhMe_2N:NMe_2Ph$, which melts at 173° to a blue liquid. It unites with acids to form soluble salts, and is precipitated from its solution by alkalis; on exposure to the air it assumes a blue colour. The *platinochloride*, $C_{16}H_{22}N_2PtCl_7$, crystallises in white needles, which are insoluble in cold water, and are reduced by alcohol and other organic substances.

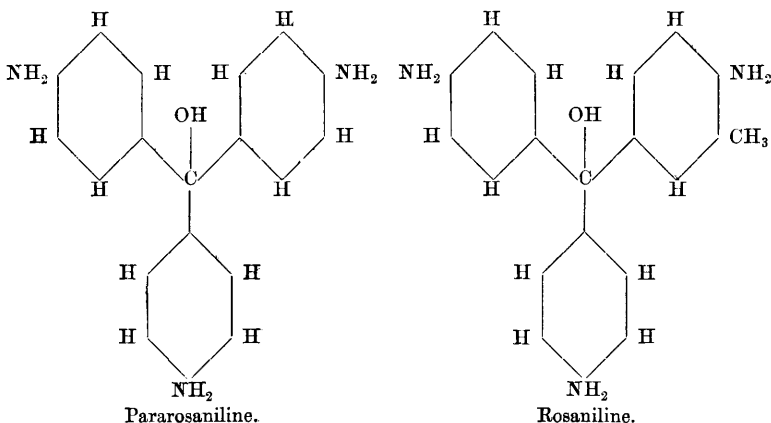
The violet dyestuff (B) greatly resembles the methyl hydrochloride of trimethylrosaniline described by Hofmann (*Ber.*, **6**, 352), but differs from the latter in its complete insolubility in a solution of liver of sulphur of sp. gr. 1.16. It appears to be formed by the oxidation of a portion of the tetramethyldiphenyldiamine produced in the same reaction, and would therefore have the constitution



This is confirmed by the fact that it can be obtained directly from tetramethyldiphenyldiamine. T. C.

Rosaniline. By E. and O. FISCHER (*Ber.*, **13**, 2204—2207).—The authors have on a previous occasion (*Ann. Chem.*, **194**, 242), shown that it is probable that only one rosaniline of the formula $C_{20}H_{21}N_3O$ exists, notwithstanding that Rosenstiehl (*Bull. Soc. Chim.*, 1879, **13**) has described three modifications having this composition. They now find, and their conclusions are confirmed by a private communication from Rosenstiehl, that their former supposition was correct, and that Rosenstiehl's ortho- and orthopara-rosanilines do not exist. Perfectly pure orthotoluidine does not give any rosaniline, as supposed by Rosenstiehl, when melted with arsenic acid and aniline, but is converted into red and yellow azo-dyestuffs.

The authors consider that the three amido-groups in rosaniline and in pararosaniline are all in the para-position, thus:—



For the formation of pararosaniline from paratoluidine proves that at least one of the amido-groups is in the para-position, whilst the decomposition of aurine into phenol and dihydroxybenzophenone (Caro and Græbe, *Ber.* **11**, 1348) shows that two of the amido-groups in rosaniline are in the para-position, since dihydroxybenzophenone is a di-para-compound (Stiedel and Gail, *Ber.*, **11**, 746; *Ann. Chem. Pharm.*, **194**; Bressler, *Ber.*, **12**, 1462). And finally the third amido-group is also proved to be in the para-position from the relation of rosaniline to the diamidotriphenylmethane obtained from benzoic aldehyde and aniline. This base when treated with nitrous acid gives dihydroxytriphenylmethane, which under the action of alkalis yields dihydroxybenzophenone, and therefore contains two para-amido-groups (Doebner, *Ber.*, **12**, 1462). The paranitro-derivative of diamidotriphenylmethane is obtained by the condensation of paranitrobenzaldehyde with aniline, and as this nitro-compound gives leucaniline (O. Fisher and P. Grieff, *Ber.*, **13**, 669) on reduction, it follows that the third amido-group of rosaniline is also in the para-position. T. C.

Nomenclature of some Azo-compounds. By K. HEUMANN (*Ber.*, **13**, 2023—2027).—The author discusses the varied nomenclature of the diazo-compounds, and the confusion which is likely to arise from a want of uniformity. He makes the following suggestions:—

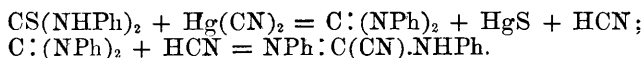
1st. There is no sufficient ground for changing the names azobenzene, azotoluene, &c., to azodiphenyl, &c., which should be reserved for the diphenyl derivatives.

2nd. In substituted azo-compounds the whole number of atoms or atom-groupings, (Cl, NO₂, SO₃H, &c.), entering into the molecule should be included in the name and not half the number. Thus the compound C₆H₄(SO₃H)N.N(SO₃H)C₆H₄ should be called azobenzenedisulphonic acid, and not azobenzenesulphonic acid.

3rd. In mixed and unsymmetrical substituted compounds the word azo should come between the names of the hydrocarbon-radicals combined by the grouping N:N. Thus, for instance, phloroglucinol-azobenzenesulphonic acid.

V. H. V.

Hydrocyanarbodiphenylimide. By A. LAUBENHEIMER and R. GÖRING (*Ber.*, **13**, 2155—2159).—This compound is obtained by boiling diphenylthiocarbamide (1 mol.) with an alcoholic solution of mercuric cyanide (1 mol.) until mercuric sulphide is no longer precipitated. In this reaction, carbodiphenylimide is first formed, and this then combines with a molecule of hydrocyanic acid to form hydrocyanarbodiphenylimide, thus:—



This is confirmed by the fact that the compound may also be obtained by the action of hydrocyanic acid on a *freshly* prepared solution of carbodiphenylimide.

Hydrocyanarbodiphenylimide crystallises in pale yellow needles or prisms (m. p. 137° uncorr.), according to the solvent employed. It is easily soluble in alcohol, glacial acetic acid, ether, and benzene, sparingly soluble in light petroleum, and insoluble in water. On warming with strong sulphuric acid it gives a red solution, which remains clear when water is added. A few drops of the sulphuric acid solution added to a large quantity of water give, on addition of soda, a deep blue liquid, the colour of which gradually disappears. When hydrocyanarbodiphenylimide is warmed with hydrochloric acid it gives aniline, oxalic acid, and ammonia.

T. C.

Quinonechlorimide and similar Substances. By A. HIRSCH (*Ber.*, **13**, 1903—1911).—Schmitt and Bennewitz, in 1875, obtained by the action of calcium hypochlorite on paramidophenol a body of the composition C₆H₄ONCl, which they (doubling this formula) regarded as dichlorinated azophenol. The author's investigation of this body has led him to the conclusion that it is not a chlorazophenol but

a chlorimide of quinone, C₆H₄ $\begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{NCl} \end{array}$. He obtains it by adding a strong solution of bleaching powder to an aqueous solution of paramido-

phenol hydrochloride, with continual stirring, until the colour of the liquid suddenly changes from violet to yellow. The magma of crystals thereby produced is then agitated with ether, which takes up the chlorimide, and leaves it in the crystalline state on evaporation.

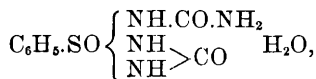
Quinonechlorimide forms golden or amber-yellow crystals with curved faces, easily cleavable in one direction, and probably triclinic. It has a distinct odour of quinone, and like that substance dissolves easily in ether, alcohol, acetic acid, chloroform, and benzene, and sparingly in cold water. It melts at $84.7-85^{\circ}$; under water at 83° . When heated above its melting point it explodes, but with care can be partially sublimed. Like quinone it colours the skin brown. It reacts with water at 100° to form quinone, ammonium chloride, and oxygen, this last producing brown oxidation-products with the quinone. In presence of reducing agents (hydrogen sulphide, tin and hydrochloric acid, zinc and sulphuric acid, sodium-amalgam) quinonechlorimide gives up its chlorine, and is converted into amidophenol. Sulphurous anhydride likewise reduces it, but the sulphuric acid thereby produced reacts with the amidophenol to form amidophenol-sulphonic acid. Although easily reduced, the chlorimide resists in a marked manner the action of oxidising agents and some strong acids. It dissolves in fuming nitric acid and in concentrated sulphuric acid in the cold, and on adding water is precipitated from the solutions unaltered; but if the solutions are heated or allowed to stand for a long time the chlorimide is completely decomposed.

Quinonechlorimide reacts with hydrochloric acid in the cold to form mono-, di- (?), and tri-chloramidophenol. From the last-named substance the author obtained a crystalline trichlorophenol melting at $54.1-54.5^{\circ}$, and boiling without decomposition at $248.5-249.5^{\circ}$ (uncorr.); insoluble in water, soluble in alcohol, ether, and benzene.

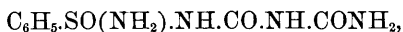
Quinonedichlorodiimide.—Krause (*Ber.*, **12**, 47) obtained by the action of calcium hypochlorite on paraphenylenediamine a body of the formula $C_6H_4N_2Cl_2$, which, from its close resemblance in properties to that described above, the author believes to be quinonedichlorodiimide.

Naphthoquinonechlorimide.—Amidonaphthol hydrochloride, when treated with solution of bleaching powder in the manner described above, yields a body which appears from analysis to be a molecular combination of naphthoquinone with naphthoquinonechlorimide. It forms yellow or pale-brown crystals, dissolves sparingly in water, melts at 35° , and explodes at 130° . J. R.

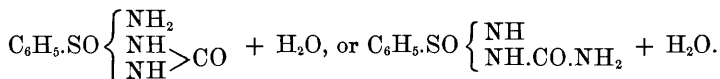
Action of Sulphonic Chlorides on Urea. By S. U. ELANDER (*Bull. Soc. Chim.* [2], **34**, 207—209).—When 1 mol. benzenesulphonic chloride and 2 or 3 mols. urea are heated at 100° , hydrochloric acid is evolved, and the mass solidifies. On dissolving the mass in hot water and cooling the solution, colourless crystals are obtained of the composition, $C_6H_5.SO.N_4H_5C_2O_2 + H_2O$. This body may have the constitution—



in which case it is analogous to pyruvil or allantoin, or its constitution may be similar to that of biuret,



which is probable, since with potash solution and copper sulphate, it gives a red colour. At a higher temperature than the above, carbonic anhydride is evolved, and the reaction gives rise to a compound either of the constitution—



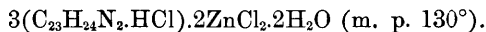
α -Naphthalenesulphonic chloride gives with urea the compound $\text{C}_{10}\text{H}_7\text{SON}_4\text{H}_5(\text{CO})_2 + \text{H}_2\text{O}$, which forms globular masses.

L. T. O'S.

Compounds of Benzotrichloride with Phenols and Tertiary Aromatic Bases. By O. DOEBNER (*Ber.*, **13**, 2222—2229).—This is a continuation of the author's previous investigations (*Ber.*, **11**, 1236; **12**, 1462; **13**, 610) on this subject.

Malachite green, $\text{PhCOH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, obtained by the action of benzotrichloride on dimethylaniline, and after purification by means of the oxalate, crystallises in colourless warty crystals (m. p. 132°). It melts under hot water, but is only sparingly soluble therein; it is easily soluble in alcohol with a green colour. In the crystalline state, it is scarcely soluble in ether, but when freshly precipitated it is easily soluble; it is also moderately soluble in carbon bisulphide and acetone, easily soluble in hot benzene and light petroleum, but less soluble in the cold. It combines with acids in several proportions to form salts. Those formed with organic acids, and the neutral salts with mineral acids, are green; its solution dyes animal and vegetable fibres an intense emerald green. Most of the salts are very soluble in water, the picrate being the least soluble. It also forms reddish-yellow acid salts with mineral acids, which are decomposed by water into the green salts. The base dissolves in acids in the cold, forming almost colourless solutions, and it is only on warming that they assume a green colour.

The *picrate*, $\text{C}_{23}\text{H}_{24}\text{N}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises from benzene in glittering golden needles. The *oxalate*, $2\text{C}_{23}\text{H}_{24}\text{N}_2\cdot 3\text{C}_2\text{H}_2\text{O}_4$, forms green prisms, which are soluble in cold and more soluble in hot water and also in alcohol. The base forms a double salt with zinc—

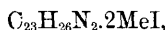


The *methyl iodide* compound, $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}\cdot 2\text{MeI}$, formed by the direct union of its constituents, crystallises in bright green leaflets (m. p. $171-172^\circ$ with decomposition), which are sparingly soluble in cold, but easily soluble in hot water. It is but little soluble in alcohol, ether, benzene, or carbon bisulphide.

Malachite green and its salts, unlike methyl green, are stable when heated with water at 200° , but on heating with concentrated hydrochloric acid at 250° , it is decomposed, giving *benzoyldimethylaniline*, $\text{PhCO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (m. p. 90°), and other basic products.

When malachite green is treated with fuming sulphuric acid, it gives several sulphonic acids, of which the monacid alone has been isolated. It crystallises in green needles with a brownish-red reflection, and is very soluble in hot water, forming a green solution, but is less soluble in cold water. The sodium salt, magnesium salt, $(C_{23}H_{23}N_2SO_3)_2Mg.4Aq$, and calcium salt $(C_{23}H_{23}N_2SO_3)_2Ca.3Aq$, are described; they are all crystalline compounds. The *hexanitro-compound* of malachite green, formed by the action of fuming nitric acid on the base dissolved in glacial acetic acid, is a neutral yellowish amorphous powder, which is but sparingly soluble in the usual solvents, and is devoid of tinctorial properties.

The *hydro-base*, $C_{23}H_{26}N_2$, is obtained by the action of reducing agents on malachite green, and is a colourless compound (m. p. 101°), identical with the base obtained by O. Fischer by the action of benzaldehyde or of benzalchloride on dimethylaniline and zinc chloride (*Ber.*, **11**, 2274; **10**, 799; **12**, 1685). By oxidation it is converted into malachite green. The *methiodide* of this hydro-base,—



crystallises in colourless six-sided tables (m. p. 231° with loss of methyl iodide).

With regard to the action of benzotrichloride on other aromatic tertiary bases, it appears that the nature of the radicals combined with the nitrogen of the aniline, has little or no influence on the tinctorial character of the resulting compound, whilst this is greatly influenced by the entrance of alcohol radicals into the benzene ring of the aniline, none of the three dimethyltoluidines, for instance, give a dyestuff on combination with benzotrichloride. Other tertiary bases, not belonging to the benzene series, such as α - and β -dimethylnaphthylamine, behave differently to dimethylaniline, and do not form a dyestuff.

T. C.

Parahydroxyphenol and some Aldehydes and Alcohols derived from Quinol. By A. HANTZSCH (*J. pr. Chem.* [2], **22**, 460—476).—*Parahydroxyphenetol* (Quinol monethyl ether),—



is obtained by heating paradiazophenetol sulphate with dilute sulphuric acid for two to three hours. It crystallises from aqueous solution in thin plates of satiny lustre (m. p. 66° ; b. p. 246 — 247°). On boiling for a short time with dilute hydriodic acid, it yields quinol.

Ethoxy-hydroxy-salicylic aldehyde, $C_6H_3(OEt)(OH).CHO$ [$OEt : OH = 1 : 4$], is prepared by slowly running chloroform into a mixture of parahydroxyphenetol and soda solution at 60° . It forms thick, nearly rectangular prisms with oblique end faces (m. p. 51.5° ; b. p. 230°); it is almost insoluble in water, but readily in alcohol, ether, chloroform, &c. It gives an intense violet coloration with ferric chloride, yields crystalline compounds with the alkalis, and reduces ammoniacal silver solutions. On fusion with potash, it yields parahydroxysalicylic acid. The ethyl-group is retained in this substance with great energy:

heating with dilute halogen acids failing to effect its removal, although they readily withdraw the ethyl-group from parahydroxy-phenetol.

Acetoethoxysalicylic aldehyde, $C_6H_3(O\bar{A}c)(OEt).CHO$ [$O\bar{A}c : OEt = 1 : 4$], is prepared from the preceding substance by heating it for several hours with acetic anhydride. It crystallises in long needles, which melt at 69° , and boil with partial decomposition at 285° . The acetyl-group is readily removed by boiling with alkalis or halogen acids, whilst the ethyl-group remains combined.

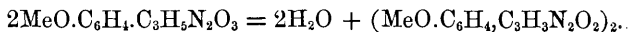
Paradiethoxysalicylic aldehyde, $C_6H_3(OEt)_2.CHO$, is prepared by adding ethyl iodide and a little absolute alcohol to the potassium derivative of ethoxyparahydroxysalicylic aldehyde. It forms fibrous groups of fine white needles (m. p. 60° ; b. p. $280-285^\circ$). On boiling with dilute nitric acid it yields *nitro-paradiethoxysalicylic aldehyde*, $C_6H_2(NO_2)(OEt)_2.CHO$, crystallising in brittle, thin, yellow needles (m. p. $129-130^\circ$).

Ethoxyparahydroxysaligenol, $C_6H_3(OEt)(OH).CH_2.OH$, is obtained by the action of nascent hydrogen on the corresponding aldehyde. It forms pale brown tables of rhombic section, which melt at 83.5° , and readily decompose at a higher temperature into a brownish resinous mass, which appears also to be formed on long contact with acids. Paradiethoxysalicylic aldehyde is scarcely attacked by sodium amalgam.

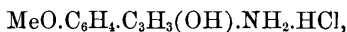
A. J. G.

Action of Nitrous Acid on Anethol. By P. TONNIES (*Ber.*, **13**, 1845—1849).—By the action of sodium nitrite on a solution of anethol in acetic acid, two compounds are obtained, namely, an addition-product, $MeO.C_6H_4.C_3H_5N_2O_3$, which gives anisic acid on oxidation, and on reduction with tin and hydrochloric acid a hydrochloride of the formula $MeO.C_6H_4.C_3H_5.(OH).NH_2.HCl$. It was not found possible to obtain the corresponding base.

Besides the above, a substitution-product is formed, which melts at 97° , and decomposes at 240° . It possesses the properties of an azo-compound, and on reduction with tin and hydrochloric acid, is converted into a crystalline compound, $(MeO.C_6H_4.C_3H_5)_2N_4O_3$, which forms a sulphonic acid. Bromine-derivatives of the two last-named compounds were obtained. The author considers that the substitution-product is composed of two molecules of the addition-product less 2 molecules of water thus:



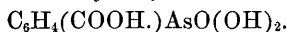
On further reduction of the substitution-product with tin and hydrochloric acid, the hydrochloride of a base,



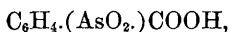
was obtained, and on removal of the hydrochloric acid the corresponding base is formed, which probably decomposes with formation of a condensation-product. The author is investigating the analogous action of sodium nitrite on styrene.

V. H. V.

Arsinobenzoic Acid. By W. LA COSTE (*Ber.*, **13**, 2176—2178).—*Parabenzarsinic Acid* or *Dihydroxylarsinobenzoic Acid*,



The potassium salt of this acid is obtained by oxidising tolylarsinic acid in potash solution (*Ann. Chem.*, **201**, 1257) with potassium permanganate. On warming this salt with strong hydrochloric acid, it gives the free acid. It crystallises in large colourless transparent tables which are only sparingly soluble in water, alcohol, and glacial acetic acid. On fusion with potash, it gives phenol; and when heated alone it loses 1 mol. of water and forms *arsinobenzoic acid*,



which is a yellow powder, and analogous to nitrobenzoic acid. The acid potassium parabenzarsinate,



crystallises in transparent triclinic tables, which on heating to 160—170° lose 2 mols. H_2O . The *silver salt*, $\text{C}_6\text{H}_4(\text{COOAg})\text{AsO}(\text{OAg})_2$, is a white amorphous precipitate, insoluble in water, but soluble in nitric acid. T. C.

Phenylamido-acetic Acid. By J. PLÖCHL (*Ber.*, **13**, 2118—2120).—Beilstein and Reinecke (*Annalen*, **136**, 169) were unable to obtain aromatic amido-acids analogous to alanine by the action of hydrocyanic and hydrochloric acids on hydramides. More recently, however, Erlenmeyer and Schäuuffeln (*Ber.*, **11**, 149) have shown that anishydramide unites directly with 2 mols. of hydrocyanic acid to form a di-imido-dinitril, which on heating with hydrochloric acid gives anisaldehyde and an amido-acid isomeric with tyrosine. The author has applied these reactions in the case of hydrobenzamide, and finds that it unites with 2 mols. of hydrocyanic acid to form the di-imido-dinitril, $\text{CHPh}(\text{CN})\text{NH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}(\text{CN})$, corresponding with that obtained from anishydramide. It forms pale-yellow crystals (m. p. 55°), which are easily soluble in ether and alcohol, insoluble in pure water, but somewhat soluble in water containing hydrocyanic acid. On warming the free compound, or better, the hydrochloride, with strong hydrochloric acid and afterwards with water, benzaldehyde and phenylamido-acetic acid are produced. T. C.

Synthesis of Cinnamic and Phenyl-lactic Acids from Ethyl Malonate. By M. CONRAD (*Ber.*, **13**, 2159—2161).—Ethyl chloromalonate reacts in the cold with an alcoholic solution of sodium ethylate to form the ethyl salt of *sodium-chloromalonic acid*, $\text{CClNa}(\text{COOEt})_2$, which, on the addition of benzyl chloride, gives the ethyl salt of *benzyl-chloromalonate*, $\text{CH}_2\text{Ph}\cdot\text{CCl}(\text{COOEt})_2$. This compound is a colourless oil (b. p. 305°, sp. gr. 1.15 at 19°), and on saponification gives cinnamic acid (m. p. 132°), and *benzylhydroxymalonic acid*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})(\text{COOH})_2$. This latter compound melts at 143° with evolution of carbonic anhydride, forming a *phenyl-lactic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ (m. p. 98°), identical with that obtained by Erlenmeyer (*Ber.*, **13**, 303), from phenylethylaldehyde and hydrocyanic acid.

On heating ethylic sodium-chloromalonate, it yields the ethyl salt of a dicarbotetracarboxylic acid, $(\text{COOH})_2\text{C}:\text{C}(\text{COOH})_2$, which crystallises in monoclinic prisms (m. p. 57° , b. p. 328° with partial decomposition), and is insoluble in water, but soluble in alcohol, ether, and benzene.

T. C.

Cinnamyl Cyanide and Cinnamyl-formic Acid. By L. CLAISEN and P. J. ANTWEILER (*Ber.*, **13**, 2123—2125).—*Cinnamic chloride*, $\text{C}_9\text{H}_7\text{OCl}$, obtained by the action of phosphorus pentachloride on cinnamic acid, is a pale-yellow crystalline mass (m. p. $35\text{--}36^\circ$, b. p. $= 170\text{--}171^\circ$ at 58 mm.). (Compare Cahours, *Annalen*, **70**, 44; and Rostowski, *ibid.*, **178**, 214).

Cinnamyl-cyanide, $\text{C}_9\text{H}_7\text{O.CN}$, is prepared by heating cinnamic chloride with silver cyanide at 100° . It crystallises in pale-yellow prisms (m. p. 114°) and less frequently in tables. It is moderately soluble in warm ether, chloroform, benzene, and carbon bisulphide, but less soluble in light petroleum. On boiling with water or potash, its solution gives cinnamic and hydrocinnamic acids.

Cinnamyl-formamide, $\text{C}_9\text{H}_7\text{O.CONH}_2$, is obtained by the action of concentrated hydrochloric on the glacial acetic acid solution of the cyanide. It crystallises in yellowish prisms or leaflets (m. p. $129\text{--}130^\circ$), which are only sparingly soluble in cold, but more soluble in hot water and also in ether, chloroform, and carbon bisulphide.

Cinnamyl-formic acid could not be obtained in the pure state, as the cyanide when treated with alkali is mostly converted into other products, and gives but a very small yield of the acid.

T. C.

Three Isomeric Amidocinnamic Acids and Carbostyryl. By F. TIEMANN and J. OPPERMAN (*Ber.*, **13**, 2056—2073).—The authors briefly refer to former researches on nitro- and amido-cinnamic acids and the relation of these compounds to members of the indigo-group. The 1 : 2 and 1 : 4 nitrocinnamic acids were prepared and separated by Beilstein and Kuhlberg's process (*Annalen*, **163**, 126); the melting point of the 1 : 4 acid was found to be $285\text{--}286^\circ$ (Beilstein and Kuhlberg, 265°); it can be heated to $280\text{--}290^\circ$ for some time without decomposition. The pure 1 : 2 acid prepared by saponification of its ethyl salt melts at 237° (Beilstein and Kuhlberg 232°); the 1 : 3 acid was prepared by Schiff's method (*Ber.*, **11**, 1782); it melts at $196\text{--}197^\circ$.

The three nitro-acids were converted into the corresponding amido-acids by reduction with ferrous sulphate in the presence of barium hydrate, and the barium salt of the amido-acid decomposed by hydrochloric acid. In the course of preparation of the 1 : 2 and 1 : 4 acid, colouring matters were observed which are probably due to the formation of members of the indigo-group.

Orthoamidocinnamic acid crystallises in needles (m. p. $158\text{--}159^\circ$), sparingly soluble in cold, moderately soluble in hot water, alcohol, and ether. Its solutions give an intense blue-green fluorescence. By treatment with concentrated acids, salts of the general formula $\text{C}_9\text{H}_9\text{NO}_2.\text{HR}$ are obtained. The hydrochloride forms hard dark prisms, easily soluble in water. The barium salt crystallises in white star-shaped prisms, which appear under the microscope as pointed tables: it contains no water of crystallisation.

Meta-amidocinnamic acid crystallises in long needles (m. p. 180—181°) of a golden-green colour, sparingly soluble in cold, more soluble in hot water, alcohol, and ether. Contrary to the observation of Limpricht (*Ber.*, **11**, 95), it was found that the hydrochloride of the acid could be obtained in a crystalline form by reduction of meta-nitrocinnamic acid with tin and hydrochloric acid. The acid salts can be prepared by the direct action of a concentrated acid on the meta-acid; the hydrochloride crystallises in colourless leaflets; the nitrate in fine colourless needles. The barium salt, $(C_9H_8NO_2)_2Ba \cdot 2H_2O$, crystallises in glistening, colourless leaflets.

Meta-amidocinnamic acid crystallises in slender, golden needles (m. p. 175—176°), sparingly soluble in cold, soluble in hot water, insoluble in alcohol and ether. It is easily decomposed with formation of a red resin. The hydrochloride crystallises in needles; easily soluble in water.

Comparison of the Actions of Copper and Zinc Sulphates, Silver Nitrate, and Lead Acetate, on strong Ammoniacal Solutions of the Three Isomeric Acids.

	Ortho-acid.	Meta-acid.	Para-acid.
Zinc sulphate	A white crystalline precipitate, insoluble in hot water	A white crystalline precipitate, sparingly soluble in hot water	A white flocculent precipitate, soluble in hot water
Silver nitrate	White curdy precipitate, soluble in hot water, and separating out on cooling	White flocculent precipitate, very sparingly soluble in hot water	White curdy precipitate, insoluble in hot water; on heating it turns brown
Copper sulphate ..	Clear green precipitate, darkening on heating	Dark green precipitate, undergoes no change on heating	Dirty brown flocculent precipitate
Lead acetate.....	Golden precipitate, which on heating melts together as a resin, then dissolves, and separates out on cooling in crystalline aggregates	White flocculent precipitate, which dissolves without change on heating, separating out on cooling in needles	White flocculent precipitate, which dissolves on heating, separating out as crystals on cooling
Concentrated sulphuric acid with nitric acid	Colours the acid a dark brown	Produces no change	Colours the acid a dark brown
Platinic chloride ..	Forms a double salt, crystallising in short pointed needles.	Forms a golden crystalline precipitate	Forms long pointed needles

The meta-acid is the most stable, and the para is the most easily decomposed of the three.

Carbostyryl, $\text{C}_6\text{H}_4\langle\frac{\text{NH}}{\text{C}_2\text{H}_2}\rangle\text{CO}$.—The authors have confirmed the observation of Chiozza (*Annalen*, **83**, 117) that carbostyryl can be prepared only by the dehydration of orthoamidocinnamic acid and not from its isomeride. They have found that the easiest process for the conversion of the ortho-acid into carbostyryl is by heating an aqueous solution of the hydrochloride of the acid with a slight excess of hydrochloric acid: $\text{C}_6\text{H}_4(\text{NH}_2).\text{C}_2\text{H}_2.\text{COOH} = \text{C}_6\text{H}_4\langle\frac{\text{NH}}{\text{C}_2\text{H}_2}\rangle\text{CO} + \text{H}_2\text{O}$. On purification, carbostyryl is obtained in silky needles melting at 196° to form a golden-coloured oil; on further heating it sublimes unchanged. As carbostyryl, $\text{C}_6\text{H}_4\langle\frac{\text{NH}}{\text{C}_2\text{H}_2}\rangle\text{CO}$, is analogous

to coumarin, $\text{C}_6\text{H}_4\langle\frac{\text{O}}{\text{C}_2\text{H}_2}\rangle\text{CO}$, the oxygen-atom being replaced by an imido-grouping, the authors' attempt to convert coumarin by digestion with ammonia into carbostyryl, was unsuccessful; the action of nitrous acid on carbostyryl, however, gave rise to an odour of coumarin, but coumarin could not be isolated from the product. Baeyer and Jackson have already observed the analogy between coumarin and carbostyryl and the similarity of properties of orthocoumaric and orthoamidocinnamic acids (this *Journal*, Abstr., 1880, 406).

Separation of Ortho- from the Mixture of Ortho- and Para-amidocinnamic Acids.—Of the barium salts of the amidocinnamic acids that of the ortho is the only one sparingly soluble in water. This property can be used for the separation of the ortho- from the para-acid in the mixture obtained by the reduction of the two isomeric nitrocinnamic acids obtained by the direct nitration of cinnamic acid.

V. H. V.

Synthesis of Tropic Acid. By A. LADENBURG and L. RÜGHEIMER (*Ber.*, **13**, 2041).—The authors have previously established the connection between hydratopic, atrolactic, atropic, and tropic acids (this *Journal*, Abstr., 1880, 472). In order to effect the synthesis of tropic acid, the authors first convert acetophenone into dichlorethylbenzene, by the action of phosphorus pentachloride: $\text{Ph.COME} + \text{PCl}_5 = \text{Ph.CCl}_2\text{Me} + \text{POCl}_3$. This is then heated with an alcoholic solution of potassium cyanide, the excess of alcohol distilled off, and the residue boiled with barium hydrate; on acidifying the product with hydrochloric acid, an oil separates out, which solidifies on cooling, and may be purified by recrystallisation. The acid crystallises in small prisms (m. p. $59-62^\circ$), and is fairly soluble in hot water. The reaction is as follows:— $\text{Ph.CCl}_2\text{Me} + \text{KCN} + \text{EtOH} = \text{Ph.CMe(OEt).CN} + \text{KCl} + \text{HCl} + 2\text{Ph.CMe(OEt).CN} + \text{Ba(OH)}_2 + 2\text{H}_2\text{O} = \text{Ph.CMe(OEt).COOH} + 2\text{NH}_3$. The authors have found that atrolactic acid is converted into atropic acid by the action of hydrochloric acid; the conversion is more easily effected by using ethyl atrolactate. Atropic acid thus obtained resembles in its melting point and other properties atropic acid obtained from tropic acid. The reaction

described above has solved the problem of the synthesis of tropic acid.

V. H. V.

Preparation of α -Hydroxyuvitic Acid. By C. BÖTTINGER (*Ber.*, **13**, 1933—1935).—This acid may be obtained by reducing α -nitrouvitic acid in spirituous solution with tin and hydrochloric acid, dissolving the resulting α -amidouvic acid in dilute sulphuric acid, and adding sodium nitrite, the solution being at last heated to 100°.

α -Hydroxyuvitic acid crystallises in needles, which melt with decomposition at 278°. The *cadmium salt* dissolves freely in hot, sparingly in cold water. The *copper salt* dissolves in ammonia, with pure green colour. The *methyl salt* crystallises from hot spirit in long needles; it volatilises with steam. J. R.

Hydroxyuvitic Acid. By O. JACOBSEN (*Ber.*, **13**, 2050—2053).—The author has described a hydroxyuvitic acid (*Annalen*, **205**, 94), obtained by fused mesitol or orthohydroxymesitylenic acid with potash. This acid gave orthocresol when heated with hydrochloric acid, thus showing that it was the orthopara-acid. The author has since obtained a second hydroxyuvitic acid by the action of fused potash on a sulphamineuvitic acid, prepared by the oxidation of ortho- and para-sulphaminemesitylenic acid. But this orthopara-acid is not identical with that obtained from mesitol, for it yields not ortho- but paracresol. Hence the former acid is not ortho-para-, but diortho-hydroxyuvitic acid.

COMPARISON OF PROPERTIES OF THE HYDROXYUVITIC ACIDS.

Diorthohydroxyuvitic Acid.

Crystallises from hot water in arborescent groups of needles; more soluble in hot water than in cold.

Softens at about 230°, with partial decomposition; at 275° it is perfectly melted.

Can be sublimed unchanged, the sublimate appearing as iridescent leaflets, which change to long needles when water is poured over them.

Gives paracresol when heated with hydrochloric acid.

Its dimethyl ether melts at 79°.

Ortho-parahydroxyuvitic Acid.

Is almost insoluble in cold, and only sparingly soluble in hot water; it separates out from its solution in small, dark, rhombohedral crystals.

Begins to soften at 280°, and melts with partial decomposition at 290°.

Sublimes as a loose mass, consisting neither of needles nor leaflets.

Gives orthocresol when heated with hydrochloric acid.

Its dimethyl ether melts at 128°.

The silver salt of the ortho-para acid is more soluble than that of the diortho-acid; both acids give a red colour with ferric chloride.

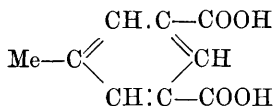
From a comparison of the properties it appears that Böttinger's

β -hydroxyuvitic acid is identical with the author's ortho-para acid, and that Böttinger's α -acid is possibly identical with the author's diortho-acid (see preceding abstract). V. H. V.

Constitution of Uvitic Acid. By C. BÖTTINGER (*Ber.*, 13, 2032—2035).—In a former research the author described, under the name of uvitic acid, a body obtained by the action of ammonia under certain conditions on pyruvic acid (this Journal, 1878, i, 32). The empirical formula, $C_8H_9NO_4$, was assigned to the acid, and to its hydrate from which the salts are derived, a formula $C_8H_{11}NO_5$. From more recent determinations the author finds that the formulæ $C_8H_7NO_4$ and $C_8H_9NO_5$ agree better with the analytical numbers obtained. Under the microscope the acid appears in the form of six-sided leaflets, and the aqueous solution gives a violet colour with ferrous sulphate. It is soluble in hot alcohol, acetic acid, phenol, glycerol, &c. Of the salts, the lead salt is the most characteristic; it is precipitated on addition of lead acetate to a solution of the calcium salt. By dry distillation with soda-lime, the acid gives only a trace of ammonia and a base which had all the characteristic properties of picoline. It would appear that uvitic acid is a picoline dicarboxylic acid, and probably has a

CH.C—COOH

constitutional formula, $\text{Me} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \text{N} \\ \text{CH:C—COOH} \end{array}$, which resembles the constitutional formula of the uvitic acid (of Finck)?



Uvitic acid is formed from amidopyruvic acid in the same way as anilineuvitic acid, $C_{20}H_{18}N_2O_4$, is from anilinepyruvic acid. Not only aniline but also other bases, such as orthotoluidine, form similar compounds. V. H. V.

Vulpic Acid. By A. SPIEGEL (*Ber.*, 13, 2219—2221).—For the purpose of determining the constitution of vulpic acid, the author has studied its decomposition-products. Vulpic acid, when boiled with dilute potash (sp. gr. 1.1), gives oxatolylic acid, $C_{16}H_{16}O_3$, carbonic anhydride, and methyl alcohol. Oxatolylic acid is a monobasic acid, and on boiling with strong potash, is further decomposed into toluene and oxalic acid (Möller and Strecker, *Annalen*, 113, 56). In addition to the carboxyl-group (COOH), oxatolylic acid contains a hydroxyl group, for it is not reduced by sodium amalgam, as it would be were the third atom of oxygen present as a ketone-group; this is further proved by the fact that on treatment with phosphorus pentachloride, it is converted into the phosphate $C_6H_{16}O_3 \cdot PO_3H_2$, which crystallises in colourless, clinorhombic prisms (m. p. 160°). The hydrogen of the hydroxyl, however, cannot be replaced by acetyl, nor is the hydroxyl-group replaced by hydrogen when treated with hydriodic acid, but the constitution of oxatolylic acid is placed beyond doubt by the following synthetical formation.

Nitril of dibenzylglycollic acid, $(\text{CH}_2\text{Ph})_2\text{C}(\text{OH})\cdot\text{CN}$, is obtained by titrating 1 mol. of dibenzyl ketone with rather more than 1 mol. of potassium cyanide, and subsequent decomposition of the product with hydrochloric acid. It crystallises in colourless rhombohedrons, which melt at 113° , and then boil with evolution of hydrocyanic acid, leaving a residue of dibenzyl ketone.

Dibenzylglycollic acid, $(\text{CH}_2\text{Ph})_2\text{C}(\text{OH})\cdot\text{COOH}$, is obtained by the action of hydrochloric acid on the nitrile at 140° . It is identical in every respect with oxatolylic acid. It melts at $156\text{--}157^\circ$ (oxatolylic acid at 154° , Möller and Strecker, *loc. cit.*, $156\text{--}157^\circ$, Spiegel), and on boiling with concentrated potash, gives oxalic acid and toluene.

T. C.

Bromorthamidoparabenzenesulphonic Acid. By L. W. ANDREWS (*Ber.*, **13**, 2126--2127).—The bromamidobenzenesulphonic acids obtained (1) directly from orthobromaniline, (2) from orthobromonitrobenzene by conversion into the sulphonic acid and subsequent reduction, (3) by the reduction of Goslich's (*Ann. Chem. Pharm.*, **180**, 101) bromonitrobenzenesulphonic acid, are all identical and have the following constitution and properties. *Bromorthamidoparabenzenesulphonic acid*, $\text{C}_6\text{H}_3(\text{Br})(\text{NH}_2)(\text{SO}_3\text{H})$ [1 : 2 : 4], crystallises in short, brilliant, four-sided, colourless prisms, which remain unchanged at a temperature of 170° . (According to Goslich it contains $1\frac{1}{2}$ mols. H_2O .) The acid is more stable than its salts and crystallises more readily; 2.55 parts of the acid dissolve in 100 parts of water at 21° . The *barium* salt, $\text{NH}_2(\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_3)_2\text{Ba}\cdot 3\text{H}_2\text{O}$, forms compact needles or white warty masses. Six parts of the dry salt dissolve in 100 parts of water at 17° . The *potassium* salt, $\text{C}_6\text{H}_3\text{Br}(\text{NH}_2)\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$, crystallises in yellow six-sided needles.

T. C.

Bromorthonitrobenzenesulphonic Acids. By L. W. ANDREWS (*Ber.*, **13**, 2127—2130).—The author infers that the bromorthonitrobenzenesulphonic acid obtained by Post and Augustin (*Ber.*, **8**, 1559) by the action of fuming sulphuric acid on bromorthonitrobenzene, and the acid obtained by Goslich (*Ann. Chem.*, **180**, 98) from parabromobenzenesulphonic acid and nitric acid, are identical and not isomeric, as Augustin (*Inaug. Diss.*, Göttingen, 1875, 19) supposed. He has compared the potassium, barium, zinc, and copper salts of the two acids, and also the acid chlorides, $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)\cdot\text{SO}_2\text{Cl}$, and the corresponding amides, $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)\cdot\text{SO}_2\text{NH}_2$ (m. p. $176\text{--}177^\circ$; Goslich found 177° for his acid), and finds them to be identical in every respect. The two acids, therefore, have the constitution $\text{C}_6\text{H}_3(\text{Br})(\text{NO}_2)(\text{SO}_3\text{H})$ [1 : 2 : 4].

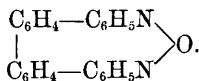
T. C.

Cymenesulphonic Acids. By A. CLAUS (*Ber.*, **13**, 2044—2045). The author shows that Spica's claim of priority with regard to the cymenesulphonic acids (this Journal, Abstr., 1880, 890) is incorrect. According to Spica, the barium salt of the second cymenesulphonic is less soluble than that of the well-known α -paracymenesulphonic acid, but according to Cratz and the author (this Journal, Abstr., 1880, 632) the barium salt of the second acid is more soluble than that of

the well-known acid. Thus the two acids in question are not identical. V. H. V.

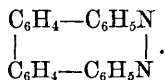
Skatole-forming Substance. By E. and H. SALKOWSKI (*Ber.*, **13**, 2217—2218).—It has been previously shown (*Ber.*, **13**, 191) that the crude hydroxy-acids, obtained during the putrefaction of albuminous bodies, contain a horny white substance, which on heating above its melting point is decomposed into skatole and carbonic anhydride. This substance is skatolecarboxylic acid, $C_9H_8N.COOH$; it crystallises from benzene in minute leaflets (m. p. 164°). T. C.

Azo-compounds of Paramononitrodiphenyl. By J. ZIMMERMANN (*Ber.*, **13**, 1960—1963).—*Azoxydiphenyl*.—This body was obtained by boiling paranitrodiphenyl with alcoholic potash. It crystallises in brilliant yellowish scales, which melt at 205° , and dissolve sparingly in acetic acid, but not in water or alcohol. Its composition agrees with the formula—



Hydrazodiphenyl, $(C_6H_4.NHPh)_2$.—This substance is produced by the action of alcoholic ammonium sulphide on azoxydiphenyl at 100° in sealed tubes. It crystallises from alcohol in small satiny plates, which melt at 247° and dissolve sparingly in alcohol and glacial acetic acid, and more freely in ether, but are insoluble in water. On standing in the air it gradually turns brown, like hydrazo-compounds generally.

Azodiphenyl.—The author has obtained this body (1) by the action of sodium-amalgam on nitrodiphenyl in ethereal solution; (2) by the oxidation of hydrazodiphenyl; and (3) by the dry distillation of hydrazodiphenyl, whereby it is resolved into azodiphenyl and amidophenyl, just as hydrazobenzene is split up into azobenzene and aniline. The second of these methods was found to answer best, the oxidation being conveniently effected by adding an alcoholic solution of ferric chloride to hydrazodiphenyl dissolved in hot alcohol. The red pulverulent precipitate thereby produced crystallises from benzene in orange-red laminæ, easily soluble in ether, but insoluble in water, alcohol, and acetic acid. It melts at $249-250^\circ$, and agrees in composition with the formula—



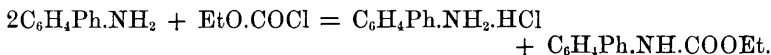
J. R.

Derivatives of Paramidodiphenyl (Xenylamine). By J. ZIMMERMANN (*Ber.*, **13**, 1963—1969).—*Diodiphenylthiocarbamide*, $SC(NH.C_6H_4Ph)_2$.—When dry monamidodiphenyl, dissolved in absolute alcohol, is heated with excess of carbon bisulphide and a little soda, an abundant evolution of hydrogen sulphide takes place, and the liquid deposits crystals of a compound which is nearly insoluble in all liquids. All attempts to recrystallise it having failed, it was

purified by boiling with alcohol and repeated washings with ether. It forms brilliant colourless laminæ, melting at 228° , and closely resembling diphenylthiocarbamide.

Diphenylthiocarbimide, $\text{SC} : \text{N} \cdot \text{C}_6\text{H}_4\text{Ph}$.—Produced by distilling the compound just described with phosphoric anhydride. It crystallises from ether in long white needles, which melt at 58° , gradually turn yellow in the air, and have the characteristic odour of thiocarbimides. This substance is isomeric with Hofmann's benzenylamidophenylmercaptan (*Ber.*, **12**, 2359; this Journal, 1880, Abstr., 885).

Diphenylurethane.—Paramidodiphenyl in ethereal solution reacts briskly with ethyl chlorocarbonate, even in the cold, in the following manner:—



The second of these products (diphenylurethane) crystallises from ether in colourless microscopic needles, which melt at 100° and soon turn brown in the air.

Phenylphenylene-glycocine, $\text{C}_6\text{H}_4\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$.—Obtained by evaporating an ethereal solution of amidodiphenyl (2 mols.) and monochloroacetic acid (1 mol.), and boiling the amidodiphenyl monochloroacetate thus formed with water. It crystallises from hot water in colourless laminæ, which dissolve easily in alcohol and ether.

Ethyl Salt of Phenylphenylene-glycocine, $\text{C}_6\text{H}_4\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOEt}$.—Formed on heating amidodiphenyl with ethyl monochloroacetate. It crystallises from weak spirit in matted white needles, melting at 95° .

Formylamidodiphenyl, $\text{C}_6\text{H}_4\text{Ph} \cdot \text{NH} \cdot \text{COH}$.—Obtained by digesting amidodiphenyl with ethyl formate in sealed tubes at 100° . It crystallises in small colourless needles (m. p. 172°), and dissolves in alcohol and ether, but only very slightly in water.

Benzoylamidodiphenyl, $\text{C}_6\text{H}_4\text{Ph} \cdot \text{NH} \cdot \text{Bz}$.—Formed by the action of benzoic chloride on amidodiphenyl. First prepared by H. Luddens (this Journal, 1875, 1258), whose statements respecting it are confirmed by the author, who, however, found the melting point to be 230° , and not 226° as stated by Luddens. J. R.

α - and β -Naphthylphenylamine. By J. STREIFF (*Ber.*, **13**, 1851—1854).— α -Naphthylphenylamine, $\text{C}_{10}\text{H}_7 \cdot \text{NHPh}$, was prepared by heating aniline (1 mol.) with naphthylamine hydrochloride (1 mol.). The author finds the melting point to be 42° (Girard and Vogt 60°). The hydrochloride of the base forms colourless prisms, and the picrate a brown warty mass. α -Acetylnaphthylphenylamine (m. p. 115°), and α -benzoynaphthylphenylamine (m. p. 152°) were obtained by the action of acetic and benzoic chlorides on the base. α -Tribromonaphthylphenylamine, prepared by the action of bromine on the base, forms colourless crystals (m. p. 137°) soluble in benzene, alcohol, and chloroform. α -Dinitronaphthylphenylamine, prepared by nitrating an acetic acid solution of the base, forms, after purification, a brown-red crystalline powder (m. p. 77°). A barium salt of α -naphthylphenylaminetetrasulphonic acid was prepared.

β -Naphthylphenylamine (Merz and Weith, *Ber.*, **13**, 1298; Abstr.,

1880, 813). By the action of bromine on the base, β -dibromonaphthylphenylamine is obtained; it forms white needles (m. p. 140°); by excess of bromine it is converted into tetrabromonaphthylphenylamine, forming pale-coloured needles (m. p. 198°). The author prepared a trisulphonic acid of β -naphthylphenylamine. V. H. V.

Reactions of Naphthol. By C. GRAEBE (*Ber.*, **13**, 1849—1851). Merz and Weith (*Ber.*, **13**, 1298; *Abstr.*, 1880, 813) have observed the formation of phenyl- β -naphthylamine and β -naphthylamine by the action of a dehydrating agent on mixtures of β -naphthol and aniline hydrochloride, and of β -naphthol and ammonia respectively. But phenol under the same conditions gives neither diphenylamine nor aniline. Phenol and naphthol show an exactly analogous difference of reaction with acids. Naphthol when heated with dilute sulphuric acid (1 : 1) is readily converted into its corresponding ether; and the author proposes to study the various effects of temperature, concentration, and mass on its formation. From β -naphthol, β -naphthyl ether is obtained after purification as white leaflets, melting at 105° , and distilling unchanged at higher temperatures; with picric acid, it forms a compound crystallising in orange-yellow leaflets; but phenol under the same conditions gives no trace of phenyl ether. Similarly β -naphthol with gaseous hydrochloric acid at 200 — 240° , or with aqueous solution (1.16 sp. gr.) at 200° is converted into β -naphthyl ether. V. H. V.

Action of Commercial Trimethylamine on β -Naphthol. By A. HANTZSCH (*Ber.*, **13**, 2053—2056).—By the action of commercial trimethylamine on β -naphthol, besides β -naphthylamine, there is formed about 90 per cent. dimethyl- β -naphthylamine. The ethiodide of this base forms silky leaflets, sparingly soluble in cold, more soluble in hot water and alcohol. By the action of moist silver oxide, the corresponding trimethyl- β -naphthylammonium hydrate is obtained as an alkaline, but not very corrosive liquid; by dry distillation, it is decomposed into methyl alcohol and the pure base dimethyl- β -naphthylamine (m. p. 46° , b. p. 305°), its salts are sparingly soluble; the platinumchloride is with difficulty soluble in alcohol; with bromine and nitric acid, the base forms bromo- and nitro-compounds. V. H. V.

Derivatives of Naphthol. By G. KOELLE (*Ber.*, **12**, 1953—1956).—The following compounds have been prepared by the author:—

β -Dinaphthylmethylene ether, $\text{CH}_2(\text{C}_{10}\text{H}_7\text{O})_2$, obtained by heating in the water-bath a solution of β -naphthol in caustic soda with methylene iodide and alcohol. The product crystallises from alcohol in fragile silky needles, melting at 133 — 134° .

β -Dinaphthylethylene ether, $\text{C}_2\text{H}_4(\text{C}_{10}\text{H}_7\text{O})_2$, and β -Naphthylbromomethyl ether, $\text{C}_2\text{H}_4\text{Br}.\text{C}_{10}\text{H}_6\text{O}$, formed simultaneously by the action of β -naphthol-sodium on ethylene bromide. The former crystallises in white shining laminae, insoluble in alcohol, water, and ether, but sparingly soluble in glacial acetic acid and benzene: it melts at 217° . The

latter is soluble in alcohol, and crystallises therefrom in fine laminæ, which melt at 96°.

β-Naphthylamidoethyl ether.—*β*-Naphthylbromomethylene ether when digested with alcoholic ammonia, yields a body which forms with hydrochloric acid a crystallisable salt agreeing with the formula $C_{10}H_7O.C_2H_4(NH_2).HCl + H_2O$, and forming with platinic chloride long needles of the formula, $\{C_{10}H_7O.C_2H_4(NH_2).HCl\}_2PtCl_4$. The free base has not yet been obtained pure.

β-Naphthylanilidoethyl ether, $C_{10}H_7O.C_2H_4.NHPh$, formed by the action of boiling aniline on *β*-naphthylbromomethyl ether, crystallises from alcohol in laminæ, which melt at 75°, and forms crystallisable salts with acids.

α-Dinaphthylethylene ether may be obtained in the same manner as the *β*-compound described above, although less easily. White crystalline laminæ, melting at 125–126°. J. R.

Biebrich Scarlet. By R. NIETZKI (*Ber.*, 13, 1838–1840).—By the action of *β*-naphthol on diazo-azobenzene, a brick-red powder, *β*-naphtholtetrazobenzene, is formed, which crystallises out from solvents in brown leaflets with a greenish metallic lustre (m. p. 195°). It has the constitutional formula $C_6H_4.N_2.C_6H_4.N_2.C_{10}H_7O$. By similar reactions, *β*-naphtholtetrazobenzene-sulphonic and disulphonic acids may be obtained, the sodium salts of which crystallise in deep red needles, and form the constituents of the dye known in commerce as “Biebrich scarlet.” By the action of zinc-dust or sodium amalgam on an alkaline solution of the sulphonic acids they are decomposed into amidonaphthol and amidazobenzenesulphonic acid. By heating *β*-naphtholtetrazobenzene at 60–100° with fuming sulphuric acid, both the naphthol and benzene groupings are sulphonated with formation of a blue dye. The author shows that dyes which are sulphonated only in the benzene grouping dye a dark green, whilst those sulphonated only in the naphthol, or both in the naphthol and benzene groupings dye a pure blue. V. H. V.

***β*-Naphtholdisulphonic and Dihydroxynaphthalene-disulphonic Acids.** By P. GRIESS (*Ber.*, 12, 1956–1960).—Two, and apparently only two, disulphonic acids of *β*-naphthol exist. Both are formed when *β*-naphthol is treated with two or three times its weight of concentrated or, better, fuming sulphuric acid at 100–110°. They may be separated from each other, and from the monosulphonic acid formed at the same time by taking advantage of the very unequal solubility of their barium salts. The acid forming a sparingly soluble barium salt is distinguished by the author as *β*-naphthol-*α*-disulphonic, whilst that forming an easily soluble barium salt is called *β*-naphthol-*β*-disulphonic acid.

β-Naphthol-α-disulphonic acid, $C_{10}H_5(OH)(HSO_3)_2$, obtained by carefully precipitating the base from an aqueous solution of the barium salt with sulphuric acid, crystallises in white silky needles, which deliquesce in the air. It dissolves very easily in water and alcohol, but not in ether; tastes strongly acid, and is completely carbonised at a high temperature. The barium salt, $C_{10}H_5(OH)(SO_3)_2Ba + 6H_2O$,

crystallises in needles, which are moderately soluble in hot, sparingly in cold water, and nearly insoluble in alcohol. The *sodium salt* crystallises in greenish masses of small needles, which dissolve very easily in water, but only sparingly in spirit, even when very weak. The aqueous solution precipitates basic lead acetate, but not silver nitrate.

β-Naphthol-β-disulphonic acid, obtained in the same way as the preceding, resembles it closely, but the crystals are more highly deliquescent. The *barium salt* crystallises with $8\text{H}_2\text{O}$ in very small white prisms, which are extremely soluble in cold water, but only very sparingly in weak spirit. The *sodium salt* forms white rhombic tables or prisms, very easily soluble in water and moderately soluble in weak spirit, differing markedly in this respect from the corresponding *β-α-salt*. Its solution likewise precipitates basic lead acetate.

The salts of both the foregoing acids exhibit, in aqueous solution, a blue-green fluorescence, which is intensified by addition of ammonia. Both the acids react with diazo-compounds to form very beautiful colouring matters, some of which are valuable as dyes, the *β-α-acid* yielding for the most part deep-red or violet, whilst the *β-β-acid* yields generally orange or bright red colours. These colouring matters are the subject of various patents in England and Germany.

Dihydroxynaphthalenedisulphonic acid, $\text{C}_{10}\text{H}_4(\text{OH})_2(\text{HSO}_3)_2$.—This acid is obtained by heating dihydroxynaphthalene with twice its weight of concentrated sulphuric acid in the water-bath, and is purified by crystallising the barium salt in the usual manner. It forms white needles or laminæ, very easily soluble in water and alcohol, but not deliquescent. The *barium salt* crystallises with 2 mols. of water in very small granules or microscopic laminæ, which dissolve very sparingly even in boiling water. It is not affected by hydrochloric acid.

This acid likewise yields with diazo-compounds yellow, red, and violet colouring matters, which, however, are not generally so beautiful as those obtained with the *β-naphtholdisulphonic acids*.

J. R.

Picene, a new Hydrocarbon from Peat-tar. By O. BURG (*Ber.*, 13, 1834—1837).—On submitting peat-tar to fractional distillation, after separation of the light paraffin, there is left at the last stage a hard golden-brown mass. On recrystallising this from petroleum, the hydrocarbon, picene, $\text{C}_{22}\text{H}_{14}$, is obtained in sulphur-yellow leaflets. Picene crystallises from cymene in a second form of white glistening leaflets (m. p. 345° corr.), having a blue fluorescence. Picene is insoluble in most menstrua, but dissolves sparingly in boiling acetic acid, chloroform, and benzene. The author considers that picene is probably identical with the hydrocarbon, parachrysene (m. p. $310\text{--}320^\circ$), obtained by Rasenach (*Ber.*, 6, 1401; this Journal, 1874, 259), from coal-tar, and with Graebe-Walter's hydrocarbon from American petroleum.

Picene-quinone, $\text{C}_{22}\text{H}_{12}\text{O}_2$.—Picene is converted into picene-quinone by oxidation with chromic acid mixture, and after purification from acetic acid is obtained as a dark orange-red crystalline powder insoluble in water, soluble in alcohol, benzene, and chloroform.

Dibromopicene, $\text{C}_{22}\text{H}_{12}\text{Br}_2$.—By the action of bromine on picene,

suspended in chloroform, it is converted into tribrompicene, which crystallises from xylene in white interlaced needles, insoluble in water, chloroform, and benzene, but easily soluble in boiling xylene and its higher homologues.

V. H. V.

Combination of Chloral Hydrate with Camphor. By P. CAZENEUVE and IMBERT (*Bull. Soc. Chim.* [2], **34**, 209—210).—By mixing crystallised chloral hydrate and camphor, a colourless viscous liquid is obtained with a diminution in temperature. It has a piquant taste, and an odour resembling those of chloral hydrate and camphor. It is soluble in alcohol and chloroform, insoluble in water by which it is decomposed; if, however, the water previously contains some chloral hydrate in solution, the liquid is not decomposed. At 19° it turns the plane of polarisation 40° to the right. Pure alcohol decomposes the liquid, the solution having the same rotatory power as camphor, but if the liquid be dissolved in alcohol containing a large proportion of chloral hydrate, the rotatory power of the solution is considerably less than that of camphor. These results lead the authors to the conclusion that the liquid is an unstable molecular compound similar to those of alcohol, acetic acid, and nitric acid with camphor.

L. T. O'S.

Acetyl-derivatives of Æsculin and Æsculetin. By H. SCHIFF (*Ber.*, **13**, 1950—1953).—The substance formerly described by the author as triacetæsculetin is now found to be diacetæsculetin, a fresh examination of the original preparation having confirmed Liebermann and Knietzsch's analysis of the body (*Ber.*, **13**, 1590). The discrepancy between Schiff's first result and that now arrived at is explained by the fact that he formerly estimated the acetyl by boiling the compound with water and magnesia. He has now discovered that under these circumstances æsculetin itself forms a soluble compound with magnesia: it follows, therefore, that the amount of acetyl found was too high.

For the same reason, the substance formerly described as hexacetæsculin is to be regarded as the pentacetyl derivative.

J. R.

Calycin. By O. HESSE (*Ber.*, **13**, 1816—1817).—From *Calycium chrysocephalum*, a yellow lichen which grows on the oak, birch, and fir, the author has extracted a crystalline substance, which he terms *calycin*. It forms red prisms (m. p. 240°), soluble in hot petroleum, ether, alcohol, chloroform, &c. The formula was found to be $C_{18}H_{12}O_3$. When heated with concentrated potash calycin is decomposed into α -toluic and oxalic acids, $C_{18}H_{12}O_5 + 3H_2O = 2C_8H_8O_2 + C_2H_2O_4$. Calycin stands in near relation to vulpic acid, but it is an anhydride which is converted into *calycic acid* by heating with potassium or sodium carbonates. On decomposing the barium salt with hydrochloric acid, calycic acid is obtained as a golden-yellow resin, soluble in water and ether, but it cannot be separated from the latter without partial regeneration of calycin.

V. H. V.

Optical Rotary Powers of Santonin-derivatives. By J. CARNELUTTI and R. NASINI (*Ber.*, **13**, 2208—2211).

	Specific rotation. [α] _D .	Molecular rotation. [α] _D M 100.	Sp. gr. of the substance.	Molecular volume.
Metasantonin (m. p. 136°)....	+118·76	+292·15	1·1649	211·17
Metasantonin (m. p. 160·5°) ..	+118·76	+292·15	1·1975	205·43
Santonin	-171·37	-421·57	1·1866	207·32
Metasantonide	-223·46	-549·71	1·046	235·96
Santonide	+744·61	+1831·74	1·1967	205·56
Parasantonide	+897·25	+2207·23	1·1957	205·74
Santonie acid	-70·31	-185·62	1·251	211·04
Methyl santonate.....	-52·33	-145·48	1·1667	238·27
Ethyl santonate	-45·35	-132·42	1·1481	254·33
Normal propyl santonate	-39·34	-120·38	1·1185	273·58
Allyl santonate	-39·54	-120·20	1·1434	265·88
Isobutyl santonate	-41·63	-133·22	1·1181	289·77
Parasantonie acid.....	-98·51	-260·07	1·2684	208·13
Methyl-parasantonate	-108·91	-302·77	1·1777	236·05
Ethyl-parasantonate	-99·98	-291·94	1·153	253·26
Propyl-parasantonate	-91·27	-279·29	1·1448	267·29
Santonyl chloride	+13·14	+37·12	1·1644	242·62
Santonyl bromide	-100·53	-328·73	1·4646	223·27
Santonyl iodide	-99·21	-371·05	1·3282	281·59

The following conclusions, among others, are drawn from the above results:—(1.) The anhydrides, except santonin and santonide, are dextrorotary, whilst the acids are lævorotary. (2.) Krecke's law of simple multiples in the molecular rotations holds good in the case of the santonins, but not in the case of the remaining compounds. (3.) The rotatory powers of some of these compounds, notably those of santonide and parasantonide, are greater than those of any other known substance.

The *normal propyl santonate* was prepared by passing hydrochloric acid into a solution of santonin in normal propyl alcohol; under diminished pressure it distils at 220°, and is a thick colourless syrup. *Isobutyl santonate* crystallises in needles (m. p. 67°). *Allyl santonate* crystallises in leaflets (m. p. 54—55°). *Propyl parasantonate* in colourless prisms (m. p. 113°). T. C.

Thapsia Garganica. By L. SOUBEIRAN (*J. Pharm. Trans.* [5], 1, 495—496).—The results obtained with the resins of *Thapsia garganica* and cleka, or "false thapsia," confirm those of Blanchet (this Journal, 38, 718). L. T. O'S.

Synthetical Pyridinetricarboxylic Acid. By C. BÖTTINGER (*Ber.*, 13, 2048—2050).—By the oxidation of uvitonic acid with potassium permanganate or chromic acid mixture, pyridinetricarboxylic acid is formed. It can be separated from the unoxidised uvitonic acid by solution in water, and purified by conversion into its barium salt, which is decomposed with sulphuric acid. Pyridinetricarboxylic acid crystallises in colourless, transparent, glistening tables, which lose

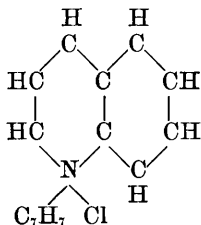
their water at 100° , melt at 244° , and become slightly brown at 220° . When heated with soda they evolve an odour of pyridine. The acid is soluble in cold and hot water, and the solution gives a violet colour with ferrous sulphate, with silver nitrate a gelatinous, with lead acetate a white, and with copper acetate a greenish-blue precipitate. With barium acetate the acid gives a bulky amorphous precipitate, which on warming is converted into slender needles, of the formula $C_8H_2Ba_3NO_6 + H_2O$. The salt decomposes on heating, with evolution of pyridine. It is not decided whether this pyridinetri-carboxylic is isomeric or identical with that obtained by Hoogewerff and van Dorp (this Journal, Abstr., 1880, 406). (Cf. Skraup, *ibid.*, 1879, 656.) V. H. V.

Synthesis of Quinoline. By C. BÖTTINGER (*Ber.*, 13, 2165—2166).—Quinoline is obtained together with water on subjecting an intimate mixture of the hydrochloride of aniluvitonic acid and soda-lime to dry distillation. 1 gram of the hydrochloride gives 1 gram of quinoline platinochloride. This reaction shows that aniluvitonic acid must be nearly related to the quinolinecarboxylic acids.

T. C.

Quinoline. By A. CLAUS and P. HIMMELMANN (*Ber.*, 13, 2045—2048).—By heating equal parts of quinoline (prepared synthetically) and benzyl chloride in sealed tubes at a temperature of 100° , a solid mass is obtained, from which the pure quinoline-benzyl chloride, $C_9H_7N.C_7H_7Cl + 3H_2O$, may be extracted in the form of large, colourless, transparent tabular crystals. The platinochloride forms dark golden needles, or a bright golden powder; both forms are very sparingly soluble in water. Quinoline-benzyl chloride forms a double compound with mercuric chloride. By the action of potash in the cold, or ammonia on warming, an oily base separates out, insoluble in water, but easily soluble in ether; this base is very unstable in light and air, and probably has the empirical formula $C_9H_6(C_7H_7)N$. The same compound is obtained by the action of silver oxide on quinoline-benzyl chloride.

In order to study better the unstable base, the authors treated its ethereal solution with hydrochloric acid to convert the base into the hydrochloride, but the hydrochloride so obtained was identical with the addition-product of quinoline and benzyl chloride. These facts are not in accordance with the accepted view of quinoline, for if quinoline-benzyl chloride has the following structural formula—



a benzylated quinoline of analogous structure is possible with the

C_7H_7 grouping replacing a hydrogen-atom; but on the other hand, it cannot be supposed that in the formation of a hydrochloride of this base there is retransposition of the C_7H_7 group from a carbon to a nitrogen-atom.

By the action of nascent hydrogen on quinoline a dark golden substance is obtained (m. p. 95°), easily soluble in ether and alcohol, insoluble in water, and crystallising with acids. The authors have also studied the action of aldehyde and amines on quinoline. As experiments on the alcoholic halogen-compounds of quinoline obtained from quinine bases, are in direct contradiction with the experiments quoted above, the authors propose to carry on a parallel research with quinoline not prepared by a synthetical process. V. H. V.

Alkaloids of Peruvian Bark. By A. CLAUS (*Ber.*, 13, 2184—2187).—From his experiments, the author concludes that cinchonidine and homocinchonidine are the same alkaloid in different conditions of purity. T. C.

Ethyl Derivatives of Cinchonidine. By A. CLAUS and M. DANNENBAUM (*Ber.*, 13, 2187—2191).—The cinchonidine employed in the following investigation had the composition $C_{20}H_{24}N_2O$, and crystallised in large compact crystals (m. p. 205°); its neutral sulphate consisted of a fine, thin, and almost gelatinous, network of needles. The *ethiodide*, $C_{20}H_{24}N_2O.EtI$, crystallises in anhydrous needles, which melt with decomposition at 249° (compare also *Ber.*, 11, 1821). *Cinchonidine methiodide*, $C_{20}H_{24}N_2O.MeI$, is very similar to the ethyl-compound, and crystallises in anhydrous colourless needles (m. p. 245 — 255° with decomposition). The ethiodide dissolves in strong hydrochloric acid on warming, and forms an intense yellow liquid, which solidifies on cooling to a mass of yellow needles (cinchonine ethiodide hydrochloride?), which, however, are not very stable. The corresponding hydriodides are obtained by the action of cinchonidine methiodide on ethyl iodide. The *diiodalkyl-compounds of cinchonidine* are best obtained by heating the moniodo-alkyl-compound with an excess of the moniodo-paraffin in sealed tubes. Their colour varies between yellow and red, and even violet, and they crystallise with 1 and sometimes 2 mols. H_2O . Iodethyl-iodmethyleinchonidine and iodmethyl-iodethyleinchonidine are isomeric, and not identical. *Ethyleinchonidine*, $C_{20}H_{23}EtN_2O$, is obtained by treating cinchonidine ethiodide with potash solution. It crystallises in transparent needles (m. p. 90°), which quickly become red on exposure to light; it is insoluble in water, but easily soluble in benzene, chloroform, &c. Its salts are so soluble in water that they cannot be obtained in the crystalline condition. The platinochloride, $C_{20}H_{23}EtN_2O.HCl.PtCl_4.H_2O$, is a bright yellow crystalline precipitate, which is soluble in hydrochloric acid, and in a large quantity of boiling water.

Ethyleinchonidine combines directly with the moniodo-paraffins. *Ethyleinchonidine ethiodide*, $C_{20}H_{23}EtN_2O.EtI$, crystallises in large colourless needles, and begins to melt with decomposition at 257° . *Ethyleinchonidine methiodide*, $C_{20}H_{23}EtN_2O.MeI$, is a similar compound, and is isomeric with methyleinchonidine ethiodide, $C_{20}H_{23}MeN_2O.EtI$.

Ethylcinchonidine ethiodide on treatment with potash gives a new base, which is isomeric and not identical with diiodethylcinchonidine.

T. C.

Methyl Derivatives of Homocinchonidine. By A. CLAUS and R. BOCK (*Ber.*, **13**, 2191—2194).—The homocinchonidine, $C_{19}H_{22}N_2O$, employed fused at 203—205°. *Homocinchonidine methiodide*,



is formed by the direct combination of methyl iodide with the free base both in alcoholic solution. It crystallises in slender colourless needles (m. p. 248°), and resembles the corresponding compound of cinchonidine in all its properties. *Homocinchonidine dimethiodide*,



is obtained by the action of methyl iodide on the preceding compound in sealed tubes at 100°. It crystallises in large prisms, which are sparingly soluble in alcohol and insoluble in ether.

Homocinchonidine methylchloride crystallises in slender silky needles, which contain 1 mol. H_2O . The anhydrous compound melts at 158° (uncorr.).

Methyl-homocinchonidine, $C_{19}H_{21}MeN_2O + H_2O$ (m. p. 75—76° uncorr.), is obtained by the action of potash on homocinchonidine methiodide. Crystallises in almost colourless tables, which assume a red colour when exposed to light. The anhydrous compound could not be obtained in the crystalline state. Its salts are very soluble in water. The platinochloride, $C_{19}H_{21}MeH_2O.2HCl.PtCl_4.3H_2O$, is a bright yellow crystalline precipitate, which is decomposed on boiling with water.

Methyl-homocinchonidine methiodide, $C_{19}H_{21}MeN_2O.MeI.2H_2O$, obtained by the direct combination of its constituents, crystallises in colourless prisms.

T. C.

Phenylhomocinchonidines. By A. CLAUS and C. BÄTCKE (*Ber.*, **13**, 2194—2196).—Two isomeric phenyl-h-cinchonidines are obtained by heating the neutral hydrochloride of h-cinchonidine with aniline (1 mol. : 1 mol.) at the boiling point of the latter.

α-Phenyl-h-cinchonidine, $C_{19}N_2PhN_2O$, is the product obtained when the action is stopped at the end of five or six hours. It is more soluble in ether than the *β*-compound, and consists of a thick oil. The *β*-compound is formed if the action is not stopped until after 60 hours' heating. It is a brown non-crystalline powder, which is insoluble in ether. Neither modification, nor the salts prepared from them, could be obtained in the crystalline state. The platinochlorides of both are yellow precipitates, $C_{19}H_{21}PhN_2O.2HCl.PtCl_4.2H_2O$. The *α*-phenyl-h-cinchonidine combines with methyl iodide to form *phenyl-homocinchonidine dimethiodide*, a reddish-brown brittle resin soluble in water.

Neutral quinine and cinchonine salts also give phenylated derivatives when heated with aniline, whilst brucine and strychnine salts do not form such compounds.

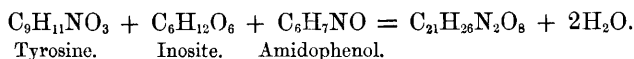
T. C.

Relation of Echitamine to Ditaïne. By O. HESSE (*Ber.*, **13**, 1841—1842).—The author (*Annalen*, **203**, 144) has shown that the

ditaine of Harnack is only impure echitamine. He has observed no formation of glucose by the action of hydrochloric acid on echitamine hydrochloride, but on filtering off the concentrated salt and testing with Fehling's solution, an abundant precipitate of cuprous oxide was thrown down. This was not due to glucose, for the reducing substance was entirely precipitated from the hydrochloric acid solution by phosphotungstic acid.

Echitamine is probably a nitrogenous base, and may perhaps be classed with apsidospermine and geisospermine. V. H. V.

A New Crystalline Decomposition-product of Albuminous Substances. By A. DANILEWSKY (*Ber.*, **13**, 2132—2136).—A crystalline compound having the composition, $C_{21}H_{26}N_2O_8$, is obtained on subjecting peptone, egg albumin, casein, blood-fibrin, or syntonin to the action of pancreas ferment. It is scarcely soluble in cold water, and quite insoluble in cold alcohol and ether, but is more soluble in hot water or hot dilute alcohol, from which it may be again separated in the form of microscopic prisms or needles. In its chemical reactions it partakes of the properties of both tyrosine and inosite; it is, however, distinguished from both these bodies by its smaller stability on long heating with water. From its general character it appears to have the following constitution:—



This is confirmed by the fact that on long boiling with dilute sulphuric acid, it splits up into a compound, $C_{15}H_{21}NO_8 (= C_9H_{11}NO_3 + C_6H_{12}O_6 - H_2O)$, exhibiting the reactions of both tyrosine and inosite, and a crystalline basic substance, probably amidophenol, which forms a well crystallised hydrochloride and platinochloride. T. C.

Metahæmoglobin. By A. JÄDERHOLM (*Zeitschr. f. Biol.*, **16**, 1—23).—Hoppe-Seyler in 1865 first gave the name metahæmoglobin to the product of the spontaneous decomposition of the blood colouring matter, and in 1875 pointed out that probably no definite body existed, but that it represented an intermediate stage in the decomposition of hæmoglobin into hæmatin and proteïds.

The results of the author's investigations show—in his opinion—that metahæmoglobin exists as a definite body, differing from hæmoglobin in its spectrum and its behaviour with reducing agents, and from hæmatin in its behaviour with reducing agents and alkalis, although its spectrum resembles that of the latter in acid solution. After referring to Sorby's researches and quoting his opinion that metahæmoglobin is a peroxyhæmoglobin, the author proceeds to examine the spectrum of metahæmoglobin in detail, and repeats his former assertion, that a pure and perfect metahæmoglobin spectrum like that of hæmatin in acid solution exhibits four absorption-bands—one band in the red, two weaker ones in the green, and nearly in the position of the bands of oxyhæmoglobin, and a fourth at the beginning of the blue, and extending to Fraunhofer's line F. He then points

out how these bands were one by one recognised and attributed to metahæmoglobin by Hoppe-Seyler, Sorby and Preyer—for reference he numbers them I, II, III, IV—No. IV the broad absorption-band in the blue is very feeble and difficult to see. He deems it highly important to decide whether Nos. II and III belong to metahæmoglobin or not. Hoppe-Seyler denies this (*loc. cit.*), and expresses the belief that they are the oxyhæmoglobin bands. This the author discusses at length.

Metahæmoglobin has, according to the author, another spectrum not mentioned by Hoppe-Seyler. When metahæmoglobin solution is made alkaline, it turns from a yellowish-brown to red, and then the spectrum exhibits only three bands, a weak one in the orange near the D line, and two in the green in the position of the oxyhæmoglobin bands, the first and second being connected by a decided absorption. The relations of these spectra to that of four-banded hæmatin are then pointed out, and the author expresses the opinion that the two bodies are closely related, but not identical, on account of their different behaviour towards alkalis and reducing agents; and from the fact that metahæmoglobin when treated with reducing agents yields the oxyhæmoglobin spectrum, the author is inclined to agree with Sorby, and regard it as a peroxyhæmoglobin. Hoppe-Seyler's objections to this theory (*Zeitschr. f. Physiol. Chem.*, 1877—78) are examined and attention drawn to the fact that various oxidising agents will convert oxyhæmoglobin into metahæmoglobin, *e.g.*, potassium permanganate, and nitrites (Gamgee).

Experiments by Hoppe-Seyler on (1) the effect of passing a stream of hydrogen for some hours through a solution of hæmoglobin. (2.) Exhaustion of a solution of hæmoglobin by the Sprengel-pump. (3.) The action of palladium saturated with hydrogen, are then examined, and the results of a repetition of the experiments with palladium given, and the author finds in every case that the resulting metahæmoglobin behaves with reducing agents exactly as metahæmoglobin prepared in any other way. He then describes his apparatus for acting on the solutions of blood to colouring matter with various reagents without admitting the air. He obtained as the result of operating with palladium-hydrogen a pure metahæmoglobin solution, which on treatment with a trace of yellow ammonium sulphide, gave the bands of hæmoglobin at once. The importance of excluding the air is dwelt upon, and a series of experiments with palladium hydrogen controlled by a second apparatus, in which no hydrogen was used is given with measurements of the spectra. These experiments the author considers render Hoppe-Seyler's conclusions untenable. From further experiments with palladium, the author concludes that its action is an indirect oxidation, and is of opinion as the general result of his observations that metahæmoglobin is a peroxyhæmoglobin. (A table of spectra accompanies the paper.)

W. N.

Physiological Chemistry.

Decomposition of Pease in the Intestine of Man. By M. RUBNER (*Zeits. f. Biol.*, 16, 118—128).—The author referring to his previous researches on the digestion of various food-stuffs, remarks that although the question is a very important one, it has not hitherto been thoroughly investigated. Strumpell and Woroschiloff made experiments in this direction, but the diet used was not purely leguminous, and he is of opinion, from previous investigations, that the admixture of other food-stuffs has an important influence on the digestion of the leguminosæ. The experiments described in the present paper were begun in the belief that the leguminosæ, although rich in nitrogen and an exceedingly cheap food, were probably very indigestible. Pease were chosen as being most to the taste of the subject of the experiment. These were decorticated and cleansed from all impurities. Objection is taken to pea-meal on the ground that it contains the husk which would vitiate the experiment. The daily ration of pease was cooked for two or three hours until quite soft, passed through a fine sieve, and taken at three meals; salt at discretion, and a litre of beer completed the diet.

The numbers of the experiments are in continuation of those previously made by the author.

Composition of the Peas.

Dry substance	87.05 per cent.
Containing nitrogen	3.91 „
Fats	1.35 „
Ash	3.05 „

Experiment 28, 16th and 17th June, 1879.

Daily Ingesta.

Peas, fresh.	Peas, dry.	N.	Fat.	Carbo- hydrates.	Ash.	NaCl.	Total dry food.
959.8	835.6	32.67	11.28	587.9	26.05	18.7	854.3

Daily Excreta (mean).

Fæces.		N.	Fat.	Ash.	Urine, c.c.	N of urine.	Uric acid.
Wet.	Dry.						
927.1	124.0	9.09	8.5	16.05	1277	21.54	1.0588

Composition of Fæces.

Nitrogen	7.33 per cent.
Fats	6.87 „
Ash	12.93 „

There was, therefore, a daily loss of—

Dry substance	14·51	per cent.
Nitrogen	27·82	„
Fats	75·35	„
Carbohydrates	6·97	„
Ash	35·82	„
NaCl	3·10	„

The fæces and urine had a strongly acid reaction, and the latter deposited large quantities of urates on standing. The results of this experiment were so much against pease as a food, that the author determined to try a smaller quantity, considering it possible that the mere mass of the diet affected its digestion; the amount was therefore reduced to 600 grams, and the result fully justified the assumption.

Experiment 29, 17th and 18th July, 1879.

Daily Ingesta.

	Peas, fresh.	Peas, dry.	N.	Fat.	Carbo- hydrates.	Ash.	NaCl.	Total dry substance.
Grams	600	511·1	20·37	7·03	357·0	15·89	14·2	535·3

Daily Excreta (mean).

	Fæces. Wet.	Fæces. Dry.	N.	Fat.	Carbo- hydrates.	Ash.	Urine, c.c.	N of urine.
	260·1	488·5	3·57	4·49	12·9	8·15	1400	17·60

Composition of Fæces.

Nitrogen	7·35	per cent.
Fats	9·26	„
Ash	16·80	„

There was, therefore, a daily loss of—

Dry substance	9·1	per cent.
Nitrogen	17·5	„
Fat	63·9	„
Carbohydrates	3·6	„
Ash	32·5	„
NaCl	1·0	„

The author then goes on to state, that the diet was theoretically ample in all its constituents for the individual experimented upon. He then raises the question as to whether the albuminoids of the leguminosæ are more or less digestible than those of wheat, and compares the result of experiments with pease with experiments on maccaroni:—

	Food.	N of food.	N of fæces.	Per cent. N lost.
Maccaroni		22·7	2·5	11·2
Pease		20·4	3·6	17·5

which is in favour of the albuminoids of wheat.

The results of a further experiment with beans are given, and may be summarised as follows:—

Daily Loss.

Dry substance	15·03 per cent.	
Fats.....	8·51	„
Carbohydrates	15·39	„
Ash	22·82	„

W. N.

Effects of Alumina Salts on Digestion. By H. A. MOTT (*Analyst*, 1880, 5, 160—161).—The results are described of feeding dogs with biscuits made with alum baking powder and also with meat mixed with precipitated hydrate of alumina, phosphate of alumina, and burnt alum respectively. Vomiting was occasioned in almost every case, and looseness of the bowels, followed by constipation. No such effects resulted from the use of cream of tartar baking powder. The artificial solution of fibrin by gastric juice in presence of the above-mentioned aluminium compounds was incomplete, and the solution of coagulated albumin was entirely prevented.

Dogs fed on food containing the aluminium compounds for four days were killed, and alumina was found in the blood, heart, liver, spleen, and kidneys.

F. C.

Researches on Tissue Change in Five Children Aged from Two to Eleven Years. By CAMERER (*Zeits. f. Biol.*, 16, 24—41).—The author's investigations comprise six series of experiments of four days each, made between September, 1878, and August, 1879; four of the children have already been the subject of experiment (*Correspondenzblatt des Würt ärztlichen Vereins*, 46, 11; and *Zeits. f. Biol.*, 1878). The results of observations on the body-weight, urine, and faeces, and analyses of the foods, are given in 14 tables, to which it is only possible here to refer on some points. The increase of body weight which may to a certain degree be regarded as an expression of the rate of growth, is somewhat irregular. In the case of the oldest child (a girl born April 1st, 1878) the daily increase of weight calculated from observations made in September and November, 1878, and January, March, April, July, September, and October, 1879, was on an average as follows:—

15·6 grams, —2·4 grams, 2·5 grams, 5·3 grams, 22·1 grams, 0·0 gram, 42 grams. The reason of this irregularity is, no doubt, the variations in the rate of flesh and fat formation which occur both in children and in adults.

The mean of all observations give the daily increase of weight per kilo. of original weight for the individual children as 0·4 gram. (eldest), 0·31, 0·27, 0·36, 0·52 (2nd year), 0·36 (3rd year).

The mean daily urea excretion was: 15·1, 14·9, 7·0, 5·9, 8·4 grams for the respective children, with some rather important variations; calculated as excretion per kilo. of body weight the 24 hours' urea gives as a mean, 0·64 gram, 0·66 gram, 0·81 gram, 0·83 gram, 1·12 gram. The urea excretion of the younger children is greater than that of the older. The greater part of the nitrogen of the food was accounted for in that of the urine and faeces, *e.g.*, 96·2, 95·7, 99·5, 94·4, and 93·3 per cent.

W. N.

Importance of Lime to the Animal Organism. By E. VOIT (*Zeits. f. Biol.*, **16**, 55—118).—The plan of the author's investigation was to observe the effect of the withdrawal of lime from the food. The importance of putting the animal on a strictly normal diet is insisted on, and the author draws attention to the fact that this is a point to which sufficient regard has not been paid by experimenters on this subject. The control over the condition of nutrition lies either in the accurate determination of the ingesta and egesta, or in comparisons with a test animal fed on precisely the same diet both as to quantity and quality and amount of lime contained in it, and which in weight, breed, and other points differs as little as possible from the actual subject of experiment. The researches were first of all made on growing animals in which the rôle of certain calcium salts is undoubtedly important.

An experiment is communicated by the author, made upon pigeons by Dr. Turek. The chief experiments were made upon dogs of a large breed.

For the first experiment three pigeons of the same brood and three weeks old were used: (*a*) was killed at the beginning of the experiment, (*b*) and (*c*) were fed on wheat washed in water, and (*b*) with spring water with pieces of mortar in it, (*c*) on distilled water only; (*b*) died on the 13th day from unknown causes, (*c*) was killed on the 30th day and was found to be well developed, only the bones appeared to be a little less capable of offering resistance than normal. The body weight had risen from 171.7 grams to 286.7 grams. With the wheat 0.362 of lime was taken in, of which 0.356 gram was found in the excreta; the bird therefore assimilated only 0.012 gram.

The chief investigations were made with dogs. A puppy of small breed, four weeks old, was fed on flesh-meal and bacon exclusively. The animal, on this diet, increased in weight and size, and on the 85th day exhibited no abnormality. At this time the first symptoms appeared, namely,—disturbances of locomotion, having their origin in defective formation of the skeleton; later marked signs of rachitis, swelling of the epiphyses, crookedness of the extremities and of the spinal column. On the 162nd day of the experiment the animal was killed. The muscles appeared well developed and all the organs normal, except the bones, which all exhibited well-marked signs of rachitis.

For the third experiment the author selected three puppies 10 days old from the same litter. For the first 20 days they were fed on milk, then for five days on a mixture of four parts flesh and one of bacon. (*A*) was killed at once, (*B*) and (*C*) fed for a further period on the same mixture, (*B*) had spring-water and bone-ash sprinkled in it, (*C*) had distilled water only. (*B*) remained normal to the end of the experiment, (*C*) early lost its liveliness and appetite, and soon exhibited symptoms of rachitis. On the 29th day both dogs were killed. (*B*) was in every respect normal, (*C*) exhibited abnormalities only in its osseous system. The bones had the same linear dimensions as those of (*B*), but were altogether more pliant and showed the characteristic swelling of the ends. Microscopical investigation indicated rachitis and not osteo-malacia. The body-weights

were at the beginning of the experiment—(A) 3,025 grams, (B) 3,235 grams, (C) 3,275 grams; at the end (B) 4,510 grams, (C) 4,710 grams.

The growth of the animals was not prejudiced by the want of lime in their food so long as that did not interfere with their appetite. The general results of these experiments agree with those of Weiske and Roloff.

Further researches were then made on the weight of the organs and the amount of dry substance they contained. The result obtained was that the increase of weight and growth of the dog (C) accorded in all respects very closely with that of the dog (B); the liver being the only exception, the increase being, in the case of dog (B), 47·5 grams, dog (C) 80·5 grams. The increase of weight of the skeleton, including cartilages, was—(B) 225·6 grams, (C) 284·9 grams. The dry weights of the organs show this relation; the bones are an exception, those of the pathological dog were considerably richer in water, viz., 71·9 per cent. against 64·9 per cent. in dog (B), and 66·2 per cent. in dog (A), the dry weight increase of the skeleton being in (B) 93·7 grams, and in (C) only 52·6 grams. The results of the analyses of the ash of the organs are given in a series of tables; they tend to the following conclusions:—That the blood of a young animal contains more lime salts than that of an adult; that the iron in the organs and blood of the dog (C) was less than in (B); the blood of (B) contained 5·44 per cent. hæmoglobin, that of (C) only 4·53 per cent.

The investigation of the bones gave the very unexpected result that the lime salts reckoned from the dry substance in (C) were not *less*, but a little *greater*, than in (B); e.g., for the dense parts of the humerus, CaO in (B) 32·77 per cent., (C) 34·62 per cent.; cancellous parts, (B) 29·23 per cent., (C) 30·96 per cent., and so also for the scapula; the bones were, however, not analysed in the fresh state, but after maceration, and the author thinking that this might in some degree account for the result, made some experiments on the bones of a pigeon, which entirely confirmed the opinion.

The author also investigated the quantity of lime necessary for the growing animal, and how far it was expressed in the food, and he comes to the conclusion that for human beings the transition from an exclusive milk diet to a mixed diet may result in a considerable deficiency of lime salts, unless the very variable quantity of lime taken in the drinking water be taken into account, which, as one of the experiments here described, shows may be sufficient for the purposes of the animal. A purely flesh diet is the poorest in lime, as Forster has shown. The author points out that the adult dog on a flesh diet excreted more lime salts than it ingested. (Perl has also determined this in his experiments on a dog in nitrogenous equilibrium—the ingested lime was 0·1215 gram and the excreted 0·3575. [See *Cent. f. d. Med. Wiss.*, 1875, 532.]).

With regard to rachitis in children, the author agrees with the generally-accepted idea that the prescription of lime in cases in which there is disturbance of the digestive powers—and these are the most numerous—cannot be of use.

W. N.

Urine after Administration of Quinine and Morphine. By A. BORNTÄGER (*Arch. Pharm.* [3], **14**, 118—120).—Urine, after administration of quinine, turns the polarised ray from 0·3 to 0·4 to the left.

The author could not discover any morphine in the urine of a person who daily took large doses of the alkaloid, whilst if this was subcutaneously injected, morphine reactions could readily be obtained from the urine. O. H.

Formation of Urea in the Animal Organism. By E. DRECHSEL (*J. pr. Chem.* [2], **22**, 476—488).—The various theories that have been suggested in relation to the formation of urea from nitrogenous food are discussed, and it is shown that most of the reactions that have been suggested require conditions with regard to temperature, &c., other than those existing in the animal organism. The author has previously shown that salts of carbamic acid are formed by the oxidation of glycocine, &c., in alkaline solution at the ordinary temperature, and he considers it probable that ammonium carbonate is the immediate source of urea, into which it can be converted by removal of the elements of water. The process of elimination must be such as to be capable of occurring in aqueous solution and at a temperature not exceeding that of the animal body, and may consist either in the direct removal of water or in the successive elimination of hydrogen and oxygen. This latter may be effected under the conditions above-mentioned in the following manner:—A solution of ammonium carbonate is submitted to a galvanic current whose direction is rapidly reversed by a self-acting commutator; the electrodes being thus rendered alternately positive and negative produce successive oxidation and reduction, and in about eight to ten hours the ammonium carbamate is found to be converted, with but slight loss, into urea. A. J. G.

Analytical Chemistry.

Apparatus for the Estimation of Nitrogen in Organic Compounds. By FLAVART (*J. Pharm.*, **1**, 503—504).—This apparatus, which is made of copper, is employed for the estimation of nitrogen in desiccated urine by means of Will and Varrentrapp's method. The plan recommended by Washburne (*Bull. Soc. Chim.*, 1876, 490) of evaporating the urine to dryness with plaster of Paris and oxalic acid is adopted in this case, but the precaution of drying the soda lime is unnecessary, since all risks of cracking from moisture coming in contact with the hot parts of the flask are avoided. L. T. O'S.

Apparatus for the Collection of Nitrogen in Elementary Analysis. By W. STAEDEL (*Zeits. Anal. Chem.*, 1880, 452—455).—Very similar to others recently described in the *Berichte*.

Simple Aspirator. By F. LUX (*Zeits. Anal. Chem.*, 1880, 455—457).—Slight modification of Bunsen's filter-pump.

Solution of Bromine as a Reagent. By L. L. DE KONINCK (*Zeits. Anal. Chem.*, 1880, 468).—Bromine-water being too dilute, and a solution of bromine in hydrochloric acid too acid for many purposes, the use of a 10 per cent. solution of potassium bromide as solvent for bromine is recommended for oxidation of As_2S_3 into H_3AsO_4 for precipitation of manganese and for detection of nickel in presence of cobalt. O. H.

Flavescin, a New Indicator. By F. LUX (*Zeits. Anal. Chem.*, 1880, 457—467).—Having observed that commercial spirit frequently assumes a strong yellow coloration on addition of alkali, the author found the reaction to be due to the presence in the spirit of certain extractive matters which had been taken up from the wood of the spirit casks. He obtained these matters—to which he gives the name *flavescin* (from *flavescere*, to turn yellow) by heating chips of oak at 220° — 260° and passing over them a current of moist air. The distillate thus obtained, containing tarry matters and acetic acid, is filtered, shaken up with ether, and the ethereal solution evaporated. The residue forms a tenacious, transparent, yellowish mass, soluble in water, alcohol, and in ether, yielding practically colourless solutions, which become yellow on the addition of alkalis or their carbonates, but not by bicarbonates, the yellow coloration being destroyed by acids, even carbonic acid.

Lux proposes flavescin as an indicator in alkalimetric titrations, for determination of caustic alkalis and bicarbonates in the presence of monocarbonates, and for the estimation of carbonic acid in all its solutions and combinations. O. H.

Analysis of Gunpowder. By A. WAGNER (*Zeits. Anal. Chem.*, 1880, 443—444).—Fresenius states that the residue obtained after extraction of the nitre from gunpowder cannot be dried at 100° without a slight loss of sulphur. Wagner, on the contrary, finds that no such loss can be observed at or below 100° . Above that temperature the residue suffers a notable diminution in weight. O. H.

Determination of Sulphur in Pyrites. By G. LUNGE (*Zeits. Anal. Chem.*, 1880, 419—431).—The author has carefully investigated the method of determining sulphur in pyrites, described by him in his *Manual of Soda Manufacture*, especially with a view to ascertain how far the various sources of error inherent to the method, and which have been pointed out by Fresenius, would counteract each other. These sources of error are the solubility of barium sulphate in free hydrochloric acid and in ferric solutions, and the contamination of the barium precipitate with ferric oxide. The author finds that considerable quantities of iron always pass into the precipitate, such contamination being avoidable only by addition of large quantities of acid, considerable loss by solubility of the barium sulphate then ensues. As a rule the errors very nearly counterbalance each other, the results being somewhat too low, but sufficiently accurate for commercial and technical analyses. He now recommends the removal of the iron by precipitation with ammonia, previous to the precipitation of the sul-

phuric acid by barium chloride. If the ferric precipitate is well washed with boiling water, it is invariably free from sulphate.

Lunge prefers the oxidation of pyrites in the moist way to fusion with nitrate and carbonate, since the latter method yields the *whole* of the sulphur as sulphate, even in the presence of lead and barium, whilst the former gives the *available* sulphur only. O. H.

Quantitative Determination of Phosphorus and Silicon in Iron and Steel. By A. E. HASWELL (*Dingl. polyt. J.*, **237**, 314—316).—This method depends on the completeness with which phosphoric acid is precipitated by molybdate of ammonium in a solution of copper nitrate, strongly acidified with nitric acid; ultimately weighing as pyrophosphate of magnesia, in the usual manner. Its simplicity and the rapidity of its execution, compared with the other methods, not only form a material point, but it has the advantage over the method of digesting the borings in a solution of double chloride of copper and ammonium, and redissolving the precipitated copper with an excess of the double salt, that it produces at once a concentrated solution, wherein the phosphoric acid may be determined, apart from the fact that a smaller quantity of the above reagent is used, hence the loss of phosphoric acid, if any, is diminished. D. B.

Estimation of Phosphoric Acid. By B. PEITZSCH and others (*Zeits. Anal. Chem.*, 1880, 444—452).—A solution of sodium phosphate was analysed in 12 different laboratories. The results obtained by simple evaporation and ignition varied from 128.4 to 129.8 mgrms. P_2O_5 in 25 c.c., whilst the figures obtained by precipitation with molybdic solution and magnesia mixture fluctuated between 127.8 and 135.7 mgrms. The authors find that the results are invariably *too high* if the magnesian chloride mixture be added *quickly* to the ammoniacal solution of the molybdic precipitate. If the magnesium solution is added *drop by drop*, with vigorous agitation, correct results are obtained, even if a very large excess be employed. The magnesia precipitate must be heated for five minutes with the blowpipe, after incineration by means of the Bunsen flame. O. H.

Detection of Zinc in Toxicological Cases. By R. OTTO (*Arch. Pharm.* [3], **14**, 100—102).—Chappuis has ascertained (*Jour. Pharm. Chim.*, [4], **27**, 403) that the whole of the zinc is to be found in the hydrogen sulphide precipitate, and not in the ammonium sulphide precipitate, if the strongly hydrochloric acid solution obtained after the destruction of the organic matter is first neutralised by means of ammonia, and then slightly acidulated with hydrochloric acid previous to treatment with hydrogen sulphide.

R. Otto confirms this observation, and recommends removing the excess of hydrochloric acid by evaporation instead of neutralisation: no trace of zinc then enters the hydrogen sulphide precipitate.

O. H.

Qualitative Separation of Cobalt from Nickel. By F. REICHEL (*Zeits. Anal. Chem.*, 1880, 468—469).—The ordinary methods of detecting cobalt in presence of much nickel, namely, precipitation with

potassium nitrite, or by means of chlorine, require much time. The following simple method of separation is founded on the difference in solubility of the hydrates in concentrated potash solutions. The hydrates are precipitated by dilute potash. From solutions containing the metals the precipitate is collected, heated with concentrated potash, and the solution, which in presence of traces of cobalt is deep blue, filtered through asbestos. O. H.

Separation and Estimation of Arsenic. By E. FISCHER (*Ber.*, **13**, 1778—1780).—The process proposed by Schneider and Fyfe for the separation of arsenic in toxicological analyses by distillation with hydrochloric acid is inexact. The author recommends the addition of ferrous chloride as a reducing agent before distilling with hydrochloric acid, the arsenic is thus separated as a trichloride from the other metals of the sulphuretted hydrogen group, including tin and antimony. The arsenic in the distillate is estimated either as the trisulphide, or by titration with iodine solution; the metals in the residue are separated from the iron, and estimated by known methods. To ensure success it is necessary that the distillate should pass over into hydrochloric acid, and that no trace of nitric acid should be present.

V. H. V.

Detection and Estimation of Arsenic. By E. REICHARDT (*Arch. Pharm.* [3], **14**, 1—23).—The author recommends, as far safer and simpler than Marsh's method, that first described by Lassaigne, consisting in the action of arsenic hydride on silver nitrate. The silver solution should be strongly acid with nitric acid, aqueous or ammoniacal solutions only partially affecting the decomposition of arseniuretted hydrogen. 0.001 mgrm. of arsenious anhydride, still furnished a plain reaction, and the author could thus readily detect arsenic in the urine of persons suffering from chronic poisoning through arsenical wall paper. The vessels used for generating the gas should not hold more than about 30 c.c., the gas itself being produced from zinc and hydrochloric acid. If the current be very slow, the whole of the arsenic is found in the silver solution, but not as arsenious acid only, as usually stated, but partially as arsenic acid, and to a very small extent in the silver precipitate. Although antimony, as is well known, also produces a blackening of the silver solution, it remains almost entirely with the zinc in the gas-generating bottle.

For the *determination* of the arsenic, the author adds a slight excess of bromine-water to the silver solution, after the whole of the arsenic has been collected in it, the end of the reaction being readily visible by the settling of the precipitate. From the filtered liquid the arsenic is precipitated as ammonium magnesium arsenate.

The quantitative experiments quoted by the author are very satisfactory, but the method appears only adapted for the determination of minute amounts of arsenic. O. H.

New Method for the Estimation of Arsenious in Presence of Arsenic Acid. By L. MAYER (*J. pr. Chem.*, **22**, 103—105).—Arsenious acid reduces ammoniacal silver solutions at a boiling heat, according to the equation, $\text{As}_2\text{O}_3 + 2\text{Ag}_2\text{O} = \text{As}_2\text{O}_5 + 2\text{Ag}_2$. The reduced

silver must be washed with warm ammonia and water containing a little sal ammoniac before weighing. As the arsenious is thus converted into arsenic acid, the latter may also be estimated. No other body capable of reducing an ammoniacal solution of a silver salt must be present. The method gives exact results. G. T. A.

Analysis of Bismuth Subnitrate. By E. BAUDRIMONT (*J. Pharm.* [5], 368—373).—The principle involved in this method is that of precipitating a given weight of bismuth subnitrate with a known volume of a standard soda-solution, and estimating the excess of alkali. The alkaline solution contains 7.407 grams NaHO per litre, of which each c.c. = 0.01 gram N_2O_5 , the acid, which is standardised to the alkali contains 9.074 grams H_2SO_4 per litre. 1 gram of the subnitrate is dissolved in 100 c.c. water, and treated with 20 c.c. alkali and 30 c.c. water, and boiled for ten minutes. The total volume is made up to 100 c.c., and the precipitated oxide filtered through a dry filter-paper. In a given volume of the filtrate the excess of alkali is determined, and from these data the amount of N_2O_5 calculated. The bismuth is estimated by drying and weighing the precipitate, or by igniting a fresh portion of the subnitrate. On igniting commercial bismuth subnitrate, a white or yellowish mass is obtained, instead of the orange residue of bismuth oxide; this is probably due to the presence of bismuth phosphate. The author is investigating the subject. L. T. O'S.

Determination of Ash in Coal and Coke. By A. WAGNER (*Zeits. Anal. Chem.*, 1880, 432—434).—Experiments are given to show that complete incineration of coal and coke can be conveniently obtained only by the use of the muffle or of the blowpipe, whilst the heat of the Bunsen flame is insufficient. O. H.

Estimation of Organic Carbon in Potable Waters. By A. SMETHAM (*Analyst* [1880], 5, 156—159).—The author acidifies 1 litre of the water with phosphoric acid, evaporates to about 50 c.c., and transfers to a small tubulated retort, the neck of which is connected with three absorption tubes, the last of which contains baryta-water. By means of an aspirator, air freed from carbonic anhydride is drawn through the tubulure of the retort and the apparatus; 20 c.c. of clear baryta-water is then filled into the first absorption-tube, the second is also charged, and the liquid in the retort is boiled until steam enters the first absorption-tube; if this causes any turbidity, the boiling is further continued until the carbonic anhydride is completely expelled, and the baryta-water is then replaced by fresh.

As soon as the retort has cooled, 1 gram of potassium dichromate, 1 gram of potassium permanganate, and 20 c.c. of sulphuric acid of 1.4 sp. gr. are introduced; the distillation is then slowly proceeded with until only 20 c.c. remain in the retort; the carbonic anhydride should be entirely absorbed in the first tube, the second serving as a tell-tale, and the third to guard against carbonic anhydride from the air. The barium carbonate precipitate is filtered off and washed, with due precautions against exposure to the air; it is then dissolved in hydrochloric acid, and the barium precipitated, and weighed as sulphate.

The points requiring attention are the perfect expulsion of carbonic anhydride from the water before beginning the oxidation process, the performance of blank experiments with the reagents used to ascertain their purity or the slight correction necessary, and the complete washing of the barium carbonate produced without allowing absorption of carbonic anhydride from the air. The distillation should proceed slowly, and the steam should be condensed in the first leg of the first U-tube.

The results obtained from known quantities of various organic substances were satisfactory; but urea yielded only 80 per cent. of its carbon unless distilled again with further addition of sulphuric acid and permanganate.

Abstractor's Note.—The author leaves out of consideration the effect produced by nitrates during the evaporation with phosphoric acid: oxidation of the organic matter present would take place to some extent, and render the carbon estimation too low. F. C.

Determination of Carbon in Water Residues. By F. PERKINS (*Analyst* [1880], 5, 124—126).—The author suggests a simplified process for determining carbon in water residues; it is a modification of Dittmar's process, suggested by Perkin's plan for decomposing nitrogen oxides, and also absorbing sulphurous anhydride evolved during the combustion of a nitrogenous organic substance.

A rather narrow combustion-tube is drawn out at one end, and charged with a mixture of potassium chromate and dichromate, and copper oxide, space being left for the introduction of the platinum boat containing the water residue behind this mixture. After the boat has been inserted, the end of the tube is connected with potash-bulbs, its anterior drawn-out end being joined to two U-tubes, the first of which contains calcium chloride, and the second soda-lime, protected from loss of moisture by a small guard-tube of calcium chloride. The combustion is carried on in a stream of air drawn through the apparatus by an aspirator, care being taken not to heat the front part of the tube strongly. The apparatus can be used repeatedly for successive combustions at short intervals without being charged afresh.

After charging the combustion-tube, the tube and its contents should be ignited in the air-stream until, when the air is passed through baryta-water, no turbidity is produced: it is then ready for use.

The results are fairly concordant when the same sample is repeatedly analysed.

Abstractor's Note.—This method is open to the objection that it leaves undetermined the organic nitrogen contained in the water residue, which is really for sanitary reasons of greater importance than the carbon determination. F. C.

Detection of Methyl Alcohol in Ethyl Alcohol. By CAZENEUVE and COTTON (*J. Pharm.* [5], 2, 361—367).—Ethyl alcohol is only slowly oxidised by potassium permanganate, whereas methyl alcohol is instantly attacked. On this property the authors have based a method for the detection and estimation of methyl alcohol in ethyl alcohol by noticing the time required for the formation of a brown

colour when a given volume of potassium permanganate solution (1 in 1,000) is added to a given volume of alcohol, and also the depth of colour which varies from a yellow to mahogany brown, according to the quantity of permanganate added.

The following table gives the coloration produced by permanganate solution (1 in 1,000) added to ethyl alcohol, containing different proportions of methyl alcohol: temperature 20°:—

Alcohol.	Time.	1 c.c. reagent.	5 c.c. reagent.	10 c.c. reagent.
Ethyl alcohol	Instant of adding	Rose colour	Rose colour	
	After 5 mins.	Yellowish rose		
	„ 10 „	Yellow rose		
	„ 15 „	Yellow, with rose shade	Mahogany brown	
	„ 20 „	Yellow		
Ethyl alcohol and 10 per cent. methyl alcohol (methylated spirits)	Instantly ..	Yellow	Yellow of burnt sugar	Mahogany brown
Ethyl alcohol and 8 per cent. methyl alcohol	Instantly ..	Yellow	Yellow of burnt sugar	Mahogany brown
Ethyl alcohol and 5 per cent. methyl alcohol	4 seconds ..	Yellow	Mahogany brown	Mahogany brown
Ethyl alcohol and 3 per cent. methyl alcohol	15 „ ..	Yellow	Mahogany pink	
Ethyl alcohol and 1 per cent. methyl alcohol	Instantly..	Pink, with shade of yellow		
	5 minutes	Yellow		

Should the alcohol contain other organic substances which are readily acted on by potassium permanganate, it should be diluted with water to separate the resins, and distilled to free it from sugar, &c.

L. T. O'S.

Wine from Raisins. By REBOUL (*J. Pharm.* [5], 2, 117—121 and 201—207).—The author discusses in detail the difficulties attending the detection of the presence of wine from raisins in wines made from the natural grapes, and has prosecuted the following research, with a view to establish a satisfactory means of attaining that object.

The method (*Moniteur Vinicole*, Jan. 17, 1880), which is founded on the left-handed rotatory power of the wine from raisins, is to be rejected, since it does not hold good for all such wines, “vin de Vourla” turning the plane 1° to the right; and moreover some wines prepared from the natural grape are lævorotatory, the rotatory power of “vin de Bon Secours” (Marseille) being -26° .

That of P. Müller based on the presence of *Saccharomyces cerevisiæ* in the dregs of natural wines adulterated with glucose or wine from raisins, has not found confirmation in the hands of the author, who

has failed to detect these germs in the wines of Thyra, Vourla, and Corinth, but found the species *Sacchavernyu*.

One distinguishing feature of the wines from raisins, but which must be accepted with some reserve, is the large proportion of gum which they contain in comparison with the natural wines; vin de Vourla containing 1·9 in 1,000, vin de Corinthe 2·4 in 1,000, whereas the wines of Ande, Hérault, Burgundy, contain only 1 in 1,000, and Chablis 0·6. However, vin de Var contains 2·03, and some others still more. Still if the amount of gum exceeds 2 in 1,000 adulteration may be suspected.

A still more decisive characteristic is the large amount of reducing sugar which the wines from raisins contain, being, according to the length of time the wine has been kept, from 5 to 3 times that usually contained in ordinary wine as is seen in the table:—

Wines from raisins 5—4 months after manu- facture.	Grams re- ducing sugar per litre.	Wines from natural grapes.	Grams re- ducing sugar per litre.
Vin de Corinthe	10·41	Vin de Var	2·8
Vin de Thyra (1).....	9·05	Vin de Fréjus	2·6
" " (2).....	11·00	Vin de Chablis	2·7
Vin de Vourla (1)	8·20	Vin de Corse (1)	1·5
" " (2)	19·00	" " (2)	1·7
		Vin de Tallone (1875)....	3·2
		Vin de Sollacaro (1877) ..	7·3
		Vin d'Olmento (1877)....	8·5

The two last examples of natural wines from Corsica show an exception to the law, as do also some Italian wines; but should the quantity of reducing sugar rise above 8 parts per litre, the wine is to be suspected.

Another means which serves to distinguish between the two classes of wines is the amount of solid extract they contain; that in wines from raisins varying from 39 to 30·5 grams per litre, and containing only about one-tenth of its weight of ash, whilst in natural wines it is only about 10 grams per litre.

Special care is required in estimating the quantity of gum present in the wine, the following process being adopted by the author:—

100 c.c. of wine are evaporated until the weight of residue is 7—8 grams, which is allowed to stand for 24 hours, when nearly all the cream of tartar separates out. It is filtered, and the residue washed four times with 5 c.c. alcohol (40—42 per cent.). To the filtrate 100—110 c.c. alcohol (92 per cent.) are added, stirring the liquid all the time to prevent the formation of viscous masses. After standing 24 hours, the gum separates out, adhering to the sides of the vessel, the liquid is filtered, and the gum washed with 25 c.c. alcohol (85 per cent.), and dissolved in water. The hot solution is filtered, and the filtrate evaporated at 100°, until its weight is constant. On ignition the amount of ash is determined. The results furnished are—

Per litre of	Crude gum.	Ash.	Gum.
	grams.	grams.	grams.
Vin de Corinthe	3·05	0·64	2·41
Vin de Thyra	3·96	1·38	2·58
Vin de Vourla	3·32	1·50	1·32

The wines of Ande, Hérault, and Burgundy contain about 1 gram per litre; exceptions are shown in the following cases:—

Per litre of	Crude gum.	Ash.	Gum.
	grams.	grams.	grams.
Vin de Sollacaro (1877)	3·70	0·55	2·15
Vin d'Olmato (1877)	5·96	1·00	4·96
Vin du Var (plastered)	4·72	2·69	2·03

It may be generally stated, however, that a greater proportion of gum than 2 in 1,000 is characteristic of wine from raisins.

The ash, about half the weight of the crude gum, consists chiefly of potassium sulphate, and some calcium phosphate.

The rotary power of the gum is $-22\cdot8^{\circ}$, and compared with that of the reducing sugar as 1 : 6·5 about.

The estimation of cream of tartar was made by a special method devised by the author, since that of Pasteur was found to yield results much below the true amount. 100 c.c. of the wine are treated in the manner described for the estimation of the gums, the cream of tartar thus obtained, after washing with alcohol, is dissolved in hot water, and the solution titrated with baryta-water (1 c.c. = 0·0015 $\text{C}_4\text{H}_5\text{K}_2\text{O}_6$). The quantity of cream of tartar remaining dissolved in the 8 grams of wine is very small, amounting to about 0·012 gram. The check experiments prove the value of this method, the results of which compared with those obtained by the ordinary method are as follows:—

	Grams of cream of tartar per litre.	
	The above method.	Ordinary method.
Vin der Corinthe	3·75	3·10
Vin de Thyra	3·82	2·30
Vin de Vourla	1·78	0·96
Vin du Var (plastered)	3·64	—
Vin de Corse „	3·40	2·1
Vin d'Olmato (1877)	1·34	—
Vin de Sollacaro (1877)	3·56	—
Vin de Bons Secours (1829) ..	1·47	0·96

Tables are given of the rotatory powers of the two classes of wine, from which it is concluded—

(1.) That the wines from raisins do not always turn the plane of polarisation to the left.

(2.) That whereas, for the most part, the wines of the South are dextrorotatory, yet exceptions are furnished in the cases of the wines of Corsica, Sollacaro, Olmeto, Sainte Lucie (1873), Tallano (1866), and Bon Secours (1829).

(3.) When the alcoholic fermentation is not complete, and sugar is left in the wine, the laevorotatory power increases with age, and sometimes the rotatory power may change from right to left, since in a mixture of glucose and levulose, the glucose is the first to undergo fermentation.

In the other constituents of the wine no very marked difference occurs between the two classes. L. T. O'S.

Estimation of the Insoluble Fatty Acids in Butter. By J. WEST KNIGHTS (*Analyst*, 1880 [5], 155—156).—The author has adopted a method for separating the insoluble from the soluble fatty acids of butter depending on the insolubility of the barium or calcium salts of the former, the corresponding salts of the latter being readily soluble. It is claimed for the new process that it obviates the difficulty experienced in washing the fatty acids with water, and in transferring them without loss to a vessel in which they can be dried and weighed. The barium salts were found most convenient to manipulate, since barium oleate shows less tendency to adhere to the sides of the vessel or to unite into a plastic mass than calcium oleate. The direct weighing of the barium salts was given up, partly from the difficulty of precipitating them free from carbonate, and also because their united weight would not give comparable results for different kinds of fat, the basicity of the fatty acids present being different.

The method is carried out as follows:—From 1 to 3 grams of clarified butter fat is saponified by heating it on the water-bath with twice its volume of alcoholic potash, and occasional addition of a few drops of boiling water for twenty minutes. The solution is diluted to 300 c.c. with cold distilled water, and is completely precipitated with barium chloride solution, the precipitate is filtered off, washed with warm water and transferred to a long stoppered tube one inch in diameter throughout, and of 250 c.c. capacity; the tube is graduated from below upwards, and furnished with a stopcock at the 50 c.c. mark. The precipitate is rinsed into this tube with water, and hydrochloric acid is added: 100 c.c. of ether is then poured in, and the tube is well shaken and allowed to stand until the two liquids separate. If the aqueous solution rises above the 50 c.c. mark it is run off through the stopcock by inclining the tube, until the ether solution extends below the stopcock when the tube is erect. If the contents of the tube before the introduction of the ether rises above the stopcock, 50 c.c. only of ether are added at first, and after shaking and allowing to stand, some of the solution is drawn off as directed above, and the remaining ether is then added and mixed by shaking.

The volume of ether solution is then noted, about 1 c.c. is run off so

as to fill the delivery tube, and a measured quantity is received into a tared flask, the ether is distilled off, and the residue of fatty acids weighed. The results are concordant and satisfactory.

F. C.

Estimation of Fatty Acids in Oils. By CARPENTIN (*J. Pharm.* [5], 1, 501—502).—50 c.c. of oil and 100 c.c. of alcohol are placed in a flask with a few drops of turmeric solution and well shaken. A solution of soda (40 grams per litre = 282 oleic acid) is dropped into the mixture until the alcoholic solution assumes a red colour, and it is then well shaken until the red colour disappears from the alcohol, taking up a fresh portion of acid from the oil. More soda solution is added, the mixture again shaken, and the process continued until the red colour of the turmeric is permanent. Since the operation is carried on in the cold, and the alcohol takes up less than $\frac{1}{1000}$ part of the oil, there is no danger of saponification.

This method may be employed for testing the acidity of alimentary, lighting, and lubricating oils.

L. T. O'S.

Analysis of Heavy Mineral Oils, of Resin and Fatty Oils, and of Resin in Oils of Commerce. (Part II). By A. RÉMONT (*J. Pharm.* [5], 2, 136—140 and 213—216. (Part I, this Journal, 38, 683).—*Qualitative Analysis.*—The specific gravity of the oil affords one of the best clues to its composition. An oil of sp. gr. less than 0.900 is certain to contain mineral oil: a sp. gr. of 0.900—0.975 shows the oil to be a more or less complex mixture, whilst a resin oil has a specific gravity above 0.975.

The oil is treated with distilled carbon bisulphide free from sulphur, whereby in all cases a clear solution is obtained, unless an alkali has been added to oil containing oleic acid, when the soap formed remains undissolved. The residue is collected, washed with carbon bisulphide, and tested for soap. The carbon bisulphide is distilled from the filtered solution, and 1 c.c. of the residue is treated with 4 c.c. alcohol at 85°; a clear solution indicates the presence of fatty acids. This solution is mixed with 50 c.c. of alcohol, added by degrees. A clear or slightly clouded liquid which becomes clear on adding a few drops of hydrochloric acid, indicates the presence of oleic acid, pure or mixed with resin. A sp. gr. 0.908 shows the oil to consist of oleic acid. A higher sp. gr. is due to the presence of resin, which may be confirmed by its action on polarised light. If the turbidity remains after addition of hydrochloric acid, and on standing oily drops separate out at the bottom of the liquid, some oil insoluble in alcohol is present.

As is often the case, 4 parts of alcohol are insufficient to dissolve 1 part of the oil; it is then necessary to agitate a larger quantity of the latter with its own volume of alcohol, and evaporate the alcoholic solution and test the residue.

Saponification.—20 grams of oil are heated at 100—110°, and treated with 15 c.c. soda solution, sp. gr. 1.324, and 10 c.c. alcohol, and evaporated nearly to dryness. 150 c.c. water are then added and the mixture boiled for half an hour.

I. An emulsion is thus produced, and if on adding water a clear oil floats on the surface a mineral or resin oil is present. On decanting the aqueous solution, and adding sulphuric acid to it, if the oil is mineral oil, no precipitate is produced. On the other hand a precipitate collecting in viscous brown drops shows the presence of resin oil. This may be confirmed with the polariscope; a sp. gr. below 0.960 indicates a mixture of mineral and resin oil.

Another means of detecting a mixture of mineral and resin oil is to carefully fractionate the oil into about 5 parts, and take the specific gravity of each fraction, which will be found to differ from those of the corresponding fractions of the pure oils.

The reaction with stannic chloride (this Journal, 38, 683) may also be applied, and if the violet colour is not very distinct in the original oil, the reaction should be tried with the separate fractions.

II. A pasty soap is formed which is soluble in water. The solution is neutralised with hydrochloric acid, and the fatty acids which separate out are melted; after cooling, a portion is treated with 4 parts of alcohol. (a.) If the solution is clear, it indicates pure fatty oil, or what is rarely the case, a mixture of fatty and resin oils. The specific gravity is an indication of the purity. Baudouin has compiled tables of the specific gravity of the fatty acids of the different oils at temperatures of 30°, and in order to compare the specific gravity of an oil at t° with the table, it is only necessary to add or subtract from the weight of a litre of the oil at t° , $0.64 \text{ gram} \times t$, according as t° is higher or lower than 30°. The specific gravity of the fatty acids of linseed oil is 0.910, for the other oils it varies from 0.892 to 0.900. If the specific gravity indicates the presence of a resin oil, a portion of the original oil is heated with alcohol, the alcoholic solution evaporated, and the residue tested with the polariscope.

(b.) A turbid solution is obtained, remaining so on addition of hydrochloric acid, oily drops separating out; this indicates the presence of mineral or resin oil. If solid flakes separate out, the presence of earth nut oil is to be suspected, since the fatty acid it contains is soluble in a small portion of alcohol, but is precipitated by excess. The flakes of arachidic acid (m. p. 73°) are soluble in soda.

III. A semi-pasty mass is obtained, and on boiling with water oily drops separate out, floating on the surface; mineral and resin oils are present. In this case the aqueous solution is decanted, and the soap precipitated with common salt. The filtered liquid has a pale colour, and on adding hydrochloric acid, an odour of fatty acid is evolved, and a slight turbidity is produced, indicating the presence of a neutral oil added to a non-saponifiable oil. If the solution is dark coloured, and on adding an acid a resinous odour is evolved, and a voluminous precipitate formed, the oil contains resin.

Quantitative Analysis.—If the oil is not completely dissolved in carbon bisulphide, the solution is filtered, and 20 grams of the residue, left on distilling off the bisulphide, are treated with 15 c.c. caustic soda solution, sp. gr. 1.324, and 15 c.c. alcohol 90—95°; after heating on a water-bath for half an hour, the mixture is allowed to stand, and the alkaline solution decanted. The saponified oil is treated with boiling water, dried, and weighed. Any oil adhering to the side of

the vessel in which the washing takes place is dissolved in ether, and after evaporation of the solvent, the residue is weighed separately. The alkaline solution is boiled to free it from alcohol, and the soap precipitated with sodium chloride (free from magnesium), carrying down with it the last traces of non-saponifiable oil. The solution decanted from this and neutralised with hydrochloric acid, gives a flocculent precipitate of resin which is collected and weighed. The soap is washed twice with salt solution, pressed between filter-paper, and allowed to stand for one or two hours in contact with 100 c.c. carbon bisulphide, when the unsaponifiable oil is dissolved, colouring the liquid yellow; this is decanted, and the soap similarly treated until the carbon bisulphide is no longer coloured. The carbon bisulphide is distilled, and the residue of unsaponifiable oil weighed; it sometimes contains small quantities of soap dissolved in it, in which case it is treated with a little water and warm carbon bisulphide, the former dissolves the soap and is separated. The unsaponifiable oil may consist of mineral or resin oils, pure or mixed; a method of separating them is still wanting.

The soap insoluble in carbon bisulphide consists of the sodium compounds of resin and fatty acids. These are converted into the barium compounds and treated with alcohol of 85°, which partially dissolves the resinous compounds; a small quantity of barium oleate goes into solution. The insoluble soap is dissolved in water and treated with caustic soda to saturation, when the soap of the fatty acids separates out, carrying down part of the imperfectly separated resin soap; the remainder is left in solution, and on saturating with sulphuric acid, a precipitate of resin is formed which is collected and weighed. The soap is dissolved in water and precipitated with barium chloride, the precipitate dried over a water-bath, and macerated with 50–60 c.c. boiling alcohol 85°: the residue is collected and washed with boiling alcohol until free from resin soap; it is then decomposed, and the fatty acid collected and weighed.

The alcoholic washings are evaporated to 50 c.c., and treated with hydrochloric acid; the precipitated resin is collected and weighed.

L. T. O'S.

Estimation of the Alkaloids in Quinine Wine. By C. SCHACHT (*Arch. Pharm.* [3], 14, 81–96).—The author dilutes 100 grams of the liquid to be analysed with double its bulk of water, and adds 150 c.c. of saturated solution of picric acid. The voluminous precipitate, after settling, is washed with picric acid solution, treated with ammonia, and the alkaloids taken up by shaking with a mixture of chloroform and absolute alcohol (4 : 1). After removal of the solvents, the alkaloid residue is acidulated with dilute sulphuric acid, the colouring matter precipitated by partial neutralisation with ammonia, and the alkaloids separated by soda, dried at 120° and weighed.

O. H.

Rapid Estimation of Atmospheric Carbonic Anhydride. By M. KAPOUSTIN (*Bull. Soc. Chim.* [2], 34, 219).—Atmospheric carbonic anhydride may be rapidly estimated by agitating the air with a solu-

tion of soda in alcohol of 90 per cent., and adding the exact quantity of water required to dissolve the precipitated sodium carbonate.

L. T. O'S.

Limits of Error in Analyses of Combustion Gases. By A. WAGNER (*Zeits. Anal. Chem.*, 1880, 434—443).—A controversial paper directed against the "Heizversuchs-station" at Munich. The author points out that it is extremely difficult to obtain average samples, since the composition of the gases varies much within the duration of the experiment.

O. H.

Quantitative Determination of Albumin by Cupric Hydrate.

By G. FASSBENDER (*Ber.*, 13, 1821—1822).—The author has examined the method proposed by Stutzer (*Ber.*, 13, 251) for the separation of albumin and other proteïds from amides and alkaloïds by cupric hydrate in the analysis of foods. In white of egg, white and black bread, sweet turnips, lupins, &c., this separation is complete. By this process the author has found other nitrogen compounds besides albumin in substances of animal origin as dry blood and so-called fish-guano. The cupric hydrate used is best prepared by precipitating a solution of copper sulphate (1 : 50), after addition of .005 vol. glycerol with a slight excess of sodium hydrate. After filtration, the precipitate is washed with a 10 per cent. glycerol solution, and kept in a closely-stoppered bottle.

V. H. V.

Analyses of Black and White Mustard. By C. H. PIESSE and L. STANSELL (*Analyst*, 1880, 5, 161—164).—The authors examined both the whole seeds and the three qualities of farina obtained therefrom by crushing and sifting.

The sulphur was precipitated as barium sulphate after oxidation with strong nitric acid.

Nitrogen was estimated by combustion with soda-lime, the fat being first removed by light petroleum, and the combustion made with the dried residue freed from fat. This preliminary treatment obviated the formation of large quantities of tar. The total nitrogen minus that contained in the potassium myronate was multiplied by 6.25 to obtain the weight of the albuminoïds.

Myrosin and albumin were extracted by prolonged treatment with cold, and finally with hot water; they were jointly estimated by evaporating a portion of the extract, and the albumin was determined in another portion after being coagulated by boiling.

The fat was extracted from the dried crushed seeds by light petroleum, and the undissolved residue after being dried and weighed was boiled successively with hydrochloric acid, soda solution, and hydrochloric acid, being washed each time with boiling water; it was then finally washed with alcohol, dried, and weighed as cellulose.

The volatile oil, consisting of allyl isothiocyanate, is formed from the brown mustard on addition of water, but admixture of some white mustard causes a greater yield to be obtained. The mixture was allowed to stand with ten times its weight of cold water for about five or six hours, this time giving the maximum production of the oil, the amount of which decreases by longer standing. The oil is distilled off

into strong ammonia as long as the escaping steam has a pungent odour; and the mixture of ammonia solution and distillate is put by in a closed vessel until the oily drops have disappeared; the liquid is then boiled for a few minutes, and the thiosinamine in solution is weighed after evaporation in a platinum dish and drying at 100°. Its weight, multiplied by 0·85344, gives the weight of allyl isothiocyanate, or, if multiplied by 3·5775, the weight of potassium myronate from which it is derivable.

Detailed analytical results are given of brown and white mustard, both for the whole seed from different sources and the three qualities of farina, of which the following numbers are averages :—

	Whole seed.		Farina.	
	White.	Brown.	White.	Brown.
Moisture	8·66	8·52	6·04	4·83
Fat.....	26·53	25·54	35·16	37·05
Cellulose	9·69	9·01	5·79	2·80
Sulphur.....	0·96	1·28	1·27	1·43
Nitrogen	4·51	4·38	4·73	4·75
Albuminoids.....	28·21	26·50	29·56	28·71
Myrosin and albumin....	4·91	5·24	6·70	6·46
Soluble matter.....	26·83	24·22	33·94	31·94
Volatile oil	0·07	0·47	0·03	1·44
Ash, total.....	4·63	4·98	4·28	4·93
Ash, soluble.....	0·65	1·11	0·44	0·92
Potassium myronate	—	1·69	—	5·15

The differences shown by the different qualities of the farina of the white seed are as follows:—The fat in the superfine is about 2 per cent. higher, and in the seconds 2 per cent. lower than the number in the table which corresponds to the fine quality; the cellulose in seconds reaches 9·34, and in superfine is only 3·90; the albuminoids and soluble matters are each about 3 per cent. lower in the seconds than the averages given above. In the brown seeds, the differences are not so marked, but the albuminoids in the seconds are about 3 per cent. below the average. The process of manufacture removes the husk and concentrates the constituents with the exception of the cellulose and water which are diminished in amount. The white seeds yield no volatile oil, and differ from the brown also by containing less sulphur and more soluble matter. The aqueous extract of white mustard yields a blood-red coloration with ferric chloride, a reaction scarcely apparent with the extract of the brown seed; further, the extract of white seed smells in a few hours strongly of sulphuretted hydrogen; that of the black smells only of the pungent mustard oil.

The ash gave the following average percentage composition: the numbers in columns 3, 4, 5 being calculated after charcoal and sand have been deducted:—

	White.	Brown.	White.	Brown.	White seed Way and Ogston, 1850.
Potash	20·08	21·41	23·81	23·59	25·78
Soda	0·19	0·35	0·23	0·38	0·33
Lime	11·40	13·57	13·49	14·95	19·10
Magnesia	9·33	10·04	11·13	11·06	5·90
Iron oxide	1·10	1·06	1·30	1·16	0·39
Sulphuric acid ..	7·11	5·56	8·48	6·12	2·19
Chlorine	0·11	0·15	0·13	0·16	trace
Phosphoric acid ..	33·87	37·20	40·22	40·99	44·97
Silica	1·06	1·41	1·25	1·55	1·31
Sand	1·88	1·38	—	—	—
Charcoal	13·98	7·57	—	—	—

The ash was obtained by incineration below redness. It consists mainly of potassium, calcium, and magnesium phosphate; there is also a trace of chlorine, but no carbonate. There is no difference between the two kinds sufficient to enable them to be distinguished by analysis.

Thiosinamine is an oily substance at 100°, but gradually solidifies when cold; it is soluble in hot water, and separates from the solution in tufts of monoclinic crystals. It is only partially oxidised when boiled with strong nitric acid. Silver nitrate and mercuric chloride yield white curdy precipitates soluble in excess of thiosinamine: platinic chloride yields an orange-yellow precipitate, soluble in hot water, insoluble in cold water and in thiosinamine, and, like the two former precipitates, soluble in alcohol.

Mayer's reagent ($\text{HgI}_2 + \text{KI}$) gives a dirty white precipitate which coheres to oily drops, slowly in the cold, but rapidly when heated. *Nessler's* solution yields a yellow precipitate, and *picric acid* precipitates strong solutions.

F. C.

Technical Chemistry.

Analysis of Ice. By A. RÜDIGER (*Arch. Pharm.* [3], **14**, 116—118).—Some of the samples analysed by the author yielded large quantities of free and albuminoid ammonia. O. H.

Manufacture of Iodine. By J. PELLIEUX and E. ALLARY (*Bull. Soc. Chim.* [2], **34**, 197—201).—The seaweeds before being burnt are piled up in large heaps and allowed to ferment, when a large quantity of liquid containing a notable quantity of iodine drains from them. This is collected, concentrated to 1.275 sp. gr., and subjected to dialysis in Dubrunfaut's osmogene. The plants deprived of their juice are ignited without further drying. By this method 9 times more

iodine is obtained than when the juice is simply evaporated and ignited without undergoing dialysis. L. T. O'S.

Comparative Examination of Samples of Magnesium Carbonate. By R. OTTO and G. GÄBLER (*Arch. Pharm.* [3], **14**, 96—99).—The carbonate made at Nauheim is purer than preparations made in England (York and Newcastle). The samples contain small quantities of chlorine, sulphuric acid, and lime. O. H.

Freiberg Lead-furnaces. (*Dingl. polyt J.*, **237**, 235—239).—A series of experiments was undertaken at the Freiberg smelting works with a view of ascertaining the consumption of fuel in the 8-shaped circular furnaces (Pilz system). A table is given in the original paper showing the composition of the gases from a number of furnaces, from which various conclusions are drawn relative to the working of the furnaces and their economical qualities. In another series of trials the heat of combustion of the gases was determined, the results indicating that these furnaces can be worked very profitably, the loss of heat being very small. D. B.

Enamelling Metals. (*Dingl. polyt. J.*, **237**, 302).—In order to enamel sheet-iron, Reichel recommends to fuse 16 pts. powdered glass, 8 pts. fluorspar, 12 pts. borax, 4 pts. nitre, 1 pt. zinc oxide, and to grind the mixture with water. This is laid on the sheets to be enamelled, and when dry burnt in a muffle. Coloured enamels are obtained by the addition of the oxides of cobalt, manganese, iron, &c., to the mixture.

Henzel and Broz have patented a method of enamelling fancy hardware. The moist enamel is laid on the core of the casting mould previously coated with graphite, and when it is dry, the iron is poured slowly into the mould so that the fused glass combines firmly with the iron. The following mixtures may be used:—

	I.	II.	III.	IV.
Silicic acid	28	34	34	34
Carbonate of sodium	11	11	11	6
Carbonate of calcium....	6	12	12	12
Pipeclay	—	—	5	—

For culinary vessels fine white moulding sand only is used, without coating the core with graphite, but the enamel is laid on a second time in the ordinary way. Daumesnil uses the following mixture:—1 kilo. borate of lead is ground with water, 12 grams crystallised chloride of platinum are dissolved in 1 litre of water, then treated with ammonia; the precipitated platinum is mixed with the borate of lead and 5 litres of water. D. B.

Residue from the Manufacture of Paraffin Oil from Schists. By G. BONG (*Bull. Soc. Chim.* [2], **34**, 147—149).—The solid residue left from the distillation of the bituminous schists of Autun gave on analysis—

C.	Fe ₂ O ₃ .	Al ₂ O ₃ .	SiO ₂ .	MgO.	K ₂ O.
5.65	3.55	27.85	63.55	1.00	4.40

The author suggests that besides the manufacture of alum, to which this residue is applied, it would, owing to its richness in potash, be most valuable as a manure, and also form a source of lithium, of which it contains notable quantities. On treating this residue with moist sulphurous anhydride, a mixture of alum and aluminium sulphate is obtained, and the aluminium silicate before hard now becomes plastic.

Besides the solid residue, large quantities of tar are obtained on treating the crude oil with soda and with acid; these are generally used in the manufacture of alum or for the preparation of superphosphates. These tar acids contain bases of the pyridine series, principally corindine, rubidine, and viridine, and also phenols, consisting principally of β - or γ -thymol and analogous bodies, with a very small proportion of α -thymol. They distil between 215–290°, those passing over first are mobile, colourless liquids, whilst the higher boiling portions are viscous and of a slight brown colour. The author points out that by proper means the distillation of these schists might be carried on so as to obtain the different products.

L. T. O'S.

Russian Fruit and Blackberry Wines. By C. O. CECHE (*Dingl. polyt. J.*, **237**, 248).—The apparatus used for the manufacture of wines in the Caucasian districts and in the Crimea, consists chiefly of presses, filters, and fermenting vats, from which the produce is at once transferred into casks or bottles. By allowing the sugar and alcohol to ferment with the juice of the fruits a product is obtained, which equals many kinds of grape wine in colour, taste, and bouquet.

When honey is used instead of sugar, a wine of peculiarly rich and pleasant bouquet is produced, resembling mead. The fruits largely used in Russia for the preparation of wine are: *Pyrus malus*, *Pyrus aucuparia*, *Ribes album*, *Ribes nigrum*, *Ribes granularia*, *Rubus idæus*, *Rubus chamæmorus*, *Rubus fruticosus*, *Fragaria vesca*, *Vaccinium Myrtillus*, *Vaccinium uliginosum*, *Vaccinium Vitis idæa*, and *Oxycoccus palustris*.

D. B.

Margarine, a Substitute for Butter and Lard. By RICHE (*J. Pharm.* [5], **2**, 125–131 and 193–195).—Margarine is manufactured from the fat of recently slaughtered oxen. The fat is separated from the membranes and heated at 45° for two hours with two pigs' or calves' stomachs for every 100 kilos., to aid the separation of the fat, which floats on the surface, and is syphoned into a vessel heated with steam, where it is mixed with 2 per cent. of salt, and finally run into vessels and allowed to cool.

This product, melting at 35–36°, is subjected to hydraulic pressure at 25–28°, when a solid cake is obtained containing about 50 per cent. of stearin, whilst the expressed portion, called *margarine* or *oleo-margarine*, is composed of margarin, stearin, and olein.

Beurre de margarine is obtained by mixing this fat with half its

weight of milk, and the same quantity of water, macerated with the udder of a cow, and the whole is coloured with annato. To avoid the inconvenience arising from the margarine having too high a melting point, which is considerably raised by over pressing, and also to bring it as near as possible to that of butter, the fat is mixed with 10–20 per cent. of oil of earth nut.

The analysis of butter and margarine has been carried out as follows. The butter is melted at 80–90° in a conical vessel, when the water and casein sink to the bottom, from which the melted fat is filtered; 10 grams are heated at 85°, with 25 c.c. alcohol, and 2 or 3 grams caustic soda are added. When the saponification is complete (in which case a few drops of water added to the mass produce no turbidity), it is evaporated to dryness, an operation requiring some time, and the residue allowed to stand over the water-bath with 100 c.c. water until all the soap has dissolved.

The solution is then treated with excess of hydrochloric acid, and heated over a water-bath until the fatty acids become perfectly clear, when they are allowed to cool, and are transferred to a flask with any clots which may be floating about in the acid solution. The contents of the flask are well washed with water until free from hydrochloric acid, and then transferred to a capsule, dried over a sand-bath and weighed.

The following results show the difference between butter and "beurre de margarine":—

	Butter.	Margarine.
Melting point of substance	About 28°	Below 25°
Melting point of fatty acids.....	35·5°	38
Casein and organic matter	0·87	0 80
Mineral matter	0·10	0·28
Water	15·40	12·60
Fatty acids insoluble in water.....	87·80	96·30

Other results are recorded, showing that butter contains 85–89 per cent. of fatty acids melting at 34·4° to 35·7°, whilst margarine contains about 95·7; m.p. 40·4–43·4°. The fatty acids of butter consist of butyric and caproic acids, which are slightly soluble in water, whilst margarine contains margaric, stearic, and oleic acids, which are quite insoluble.

Michels observes that as margarine is not subjected to a higher temperature than 50°, germs and morbid secretions are not destroyed, and consequently it is unfit for use as a food; and moreover the fact that it is often manufactured from refuse fat makes its objectionable. The first objection is applicable to butter, and for cooking operations margarine may be used with impunity.

L. T. O'S.

Saponification of Fats. (*Dingl. polyt. J.*, **237**, 205.)—According to Köning the weighed sample of fat is mixed with two equivalents of oxide of lead and the necessary quantity of water, and heated

on a water-bath for some time, the mixture being stirred occasionally and the evaporated water renewed. The saponified mass is kneaded repeatedly with hot water, the latter filtered off and evaporated at a moderate temperature. The residue is dissolved in alcohol, filtered, evaporated at a gentle heat and weighed as glycerol. The lead soap is dried and shaken up three or four times with ether, the ethereal solution is distilled off, the residue dried and weighed as oleate of lead. The residue insoluble in ether containing the stearate and palmitate of lead is decomposed with dilute hydrochloric acid, shaken up with ether, dried and weighed as solid fatty acids.

Von der Becke has subjected this method to a series of trials, and concludes from his tabulated results that the saponification with oxide of lead alone is insufficient for some fats; more accurate determinations of glycerol are obtained when the fat is saponified with potash. The high percentage of lead in the soluble lead salts, which in most cases was more than required by oleate of lead, was attributed either to the formation of basic compounds or the presence of lower fatty acids.

D. B.

Use of Methyl Alcohol in Preparing Colouring Matters. (*Dingl. polyt. J.*, **237**, 316—318).—Although by the iodide of methyl method the percentage of methyl alcohol can be determined in commercial alcohol, the method does not give any data as to the nature of the impurities, and as the purity of the alcohol forms an important part in the manufacture of aniline colours, Krämer made it his object to investigate this subject more closely. The following method was worked out, and is said to give accurate results for the determination of acetone, which forms the most injurious impurity in methyl alcohol:—10 c.c. of double-normal solution of soda are introduced into a 50 c.c. cylinder and shaken up with 1 c.c. of the alcohol to be tested; 5 c.c. double-normal solution of iodine are added, and the mixture is well agitated. The precipitated iodoform is taken up with 10 c.c. of ether. 5 c.c. of the ethereal layer (after having been measured) are evaporated on a tared watch-glass. The residue is weighed and represents iodoform, which can be readily calculated into acetone thus: 1 mol. acetone (= 58) and 6 iodine (= 127×6) give 1 iodoform = 394. For the manufacture of colouring matters, the methyl alcohol should not contain more than 1 per cent. acetone. This impurity not only hinders the methylating process giving rise to short yields, but the base thus obtained has properties which render it useless for the further development into violet.

D. B.

Analysis of Tinned Foods. By G. W. WIGNER (*Analyst* [1880], **15**, 126—128).—*Corned beef of the St. Louis Canning Company* was found to contain the following percentages:—Moisture, 52.23; albuminoid substances, 25.44, containing 4.07 of nitrogen; fat, 6.71; ash, 4.76, containing sodium chloride, 3.0, and calcium phosphate, 0.85. The meat is only moderately salted, and since bone is absent, the proportion of phosphates present is good. The moisture is about two-thirds, the fat about one-fourth, and the albuminoids about twice that present in raw beef. Its dietetic value is about twice that of boneless

fresh beef, and two and a third times that of average joints with bone: its cost would be at the rate of about $4\frac{1}{2}d.$ per pound for good sound meat.

The *cooked ox-tongues* of the same company gave 51.58 per cent. of moisture, 12.15 of albuminoids containing 1.92 of nitrogen, 7.28 of fat, and 6.24 of ash, containing 4.94 of sodium chloride; they contain less salt and more nutritive matter than ordinary dried tongues.

Tinned *tomatoes* contained 5.52 per cent. of solid matter, 10.2 being the average percentage in ripe tomatoes.

The *soups* are nutritious, but strong in taste.

Succotash is an American preparation of haricot beans, Lima beans, and maize cooked in the tin, with the addition of a little fat: it yielded on analysis 74.58 per cent. of moisture, 3.6 of albuminoid matters, containing 0.58 of nitrogen, 1.66 of cellulose, and 0.75 of ash: it is a good specimen of boiled vegetable food. F. C.

Comparative Examination of Various Kinds of Gum Arabic and of Tragacanth. By E. MASING (*Arch. Pharm.* [3], 14, 34—48).—The percentage of soluble matters in gum arabic varies from 11.6 to 86.1; of mineral matter from 2.2 to 5.9.

Gum tragacanth from various plants and localities contains from 1.7 to 8.2 per cent. of ash, and yields to water from 2.9 to 42.5 per cent. O. H.

Aqueous Varnish for Prints on Unglazed Paper. By J. M. EDER (*Dingl. polyt. J.*, 237, 242—244).—300 parts of water are boiled with 3 to 5 parts of ground roots of mountain-ash from a quarter to half an hour, and decanted.

24 parts of powdered crystallised borax, 4 parts of soda, and 100 parts powdered well bleached shellac, are added to the decoction, and the whole is again heated. The shellac dissolves after boiling a short time, forming a turbid yellow coloured liquid, which on cooling is filtered through cotton. The paper to be glazed is allowed to float in this aqueous varnish for a short time, then taken out and hung up to dry. The varnish can be advantageously used for impressions, as well as for other prints on thick paper, such as engravings on copper, maps, &c. D. B.

Destructive Action of Wood on Salicylic Acid. By H. KOLBE (*J. pr. Chem.*, 22, 112).—(Compare this Journal, 1880, 520.) The author forgot to state in his former paper that the casks were imperfectly closed, so that when all the salicylic acid had disappeared, germs from without got into the water, and it became bad. This is not the case if the casks are tightly closed. G. T. A.

General and Physical Chemistry.

Absorption Spectrum of Ozone. By J. CHAPPUIS (*Compt. rend.*, 91, 985).—The absorption spectrum of ozone presents eleven well defined dark bands. Several of these coincide partially or entirely with certain telluric bands. The author believes that ozone contributes to, if it is not the sole cause of the blue colour of the sky. R. R.

Specific Refraction and Dispersion of Isomeric Bodies. By J. H. GLADSTONE (*Phil. Mag.* [5], 11, 54—60).—The ordinary view, that the nature of the solvent has no appreciable effect on the specific refraction of a substance, is generally if not absolutely true. Thus, the specific refraction of pyrene in benzene is 0·6235, in chloroform 0·6252, and in carbon bisulphide 0·6240.

Many compounds having the same composition as regards the nature and proportion of their constituent elements, have also the same specific refraction, and yet differ considerably—(1) in their other optical properties, thus:—

	Action on polarised light.	Specific refraction.	Specific dispersion.
Tartaric acid	Active	0·3020	0·0131
Racemic acid	Inactive	0·3036	0·0143

(2.) In their molecular weights, thus:—

	Specific refraction.	Specific dispersion.
Terpenes, $C_{10}H_{16}$	0·5370	0·0302
Citrenes, $C_{10}H_{16}$	0·5475	0·0336
Cedrenes, $C_{15}H_{24}$	0·5392	0·0307
Colophene, $C_{20}H_{32}$	0·5413	0·0329

(3.) In their general chemical character (metameric compounds), thus:—

		Specific refraction.	Specific dispersion.
Propyl iodide	} C_3H_7I	{ 0·2844	0·0216
Isopropyl iodide		{ 0·2883	—
Cresol from thymol	} C_7H_8O	{ 0·5116	0·0454
Metacresol		{ 0·5091	0·0452
Benzyl alcohol		{ 0·5069	0·0415
α -Nitrobenzoic acid	} $C_7H_5NO_4$	{ 0·3994	—
β - " " "		{ 0·4004	—
Benzyl butyrate	} $C_{11}H_{14}O_2$	{ 0·4777	0·0332
" isobutyrate		{ 0·4805	0·0331
Monochlorotoluene	} C_7H_7Cl	{ 0·4807	0·0409
Benzyl chloride		{ 0·4836	0·0409

There are, however, some isomeric compounds which have very different specific refractions, thus:—

		Specific refraction.	Specific dispersion.
Aniline	$\left. \begin{array}{l} \text{C}_6\text{H}_7\text{N} \end{array} \right\}$	0.550	0.0635
Picoline		0.513 and 0.522	0.0448 and 0.0431
Acetone	$\left. \begin{array}{l} \text{C}_3\text{H}_6\text{O} \end{array} \right\}$	0.4420	0.0207
Ethyl butyrate		0.4402	0.0191
Allyl alcohol	$\left. \begin{array}{l} \text{C}_3\text{H}_6\text{O} \end{array} \right\}$	0.4734	0.0275
Carvol		0.5122	0.0355
Thymol	$\left. \begin{array}{l} \text{C}_{10}\text{H}_{14}\text{O} \end{array} \right\}$	0.5206	—
α -Nitraniline		0.4690	—
β - „	$\left. \begin{array}{l} \text{C}_6\text{H}_6\text{N}_2\text{O}_2 \end{array} \right\}$	0.5460	—
Cresyl acetate		0.4677	0.0348
Benzyl „	$\left. \begin{array}{l} \text{C}_9\text{H}_{10}\text{O}_2 \end{array} \right\}$	0.4945	0.0394
Phenyl-ethyl acetate		0.4776	—
Hydrocinna- mene acetate	$\left. \begin{array}{l} \text{C}_{10}\text{H}_{12}\text{O}_2 \end{array} \right\}$	0.5183	0.0382

Some of these form the most striking illustrations of Brühl's theory (this Journal, Abstr., 1880, 781). As regards specific dispersion ($\frac{\mu_H - \mu_A}{d}$), the following conclusions are drawn:—(1.) Where the carbon-atoms are exerting more than normal influence on the refraction of the rays of light, there is a great increase of dispersion. (2.) Where isomeric bodies have the same or nearly the same specific refraction for the line A, they have the same also for the line H. Exceptions to this rule are attributed either to experimental error or to impurity. T. C.

Optical Constants. By J. V. JANOWSKY (*Ber.*, 13, 2272—2277).—The author determined the refractive power of a large number of organic compounds for the sodium line, and has deduced the following conclusions from his experimental results:—

1. The index of refraction of organic compounds depends not only on the number but also on the arrangement of atoms in the molecule.
2. Isomeric bodies exhibit dissimilar refractive indices.
3. The refractive equivalent of an element in its compounds is variable, and depends on the nature and number of atoms in the molecule.
4. The refractive power of isomeric compounds in the aromatic series is influenced by the relative position of the radicles, both in the benzene nucleus and in the side chains. W. C. W.

Fluorescence. By S. LAMANSKY (*Ann. Chem. Phys.* [2], 11, 908—912).—A method is described for examining the phenomena of fluorescence, in which the light is allowed to fall directly on the free surface of the liquid, and not on the glass wall of the containing vessel, as is generally done. In this way the fluorescent properties of magdala red, fluoresceïn, and eosin have been investigated, with the following results:—

As regards the *fluorescent spectrum*, the spectrum begins at a defi-

nite ray for each substance, and extends into the ultra-violet, all the rays producing a uniform colour impression on the eye, that is to say, each fluorescent spectrum has a definite colour which is characteristic for any particular body. The position of the vision-telescope, however, has to be changed considerably for each Fraunhofer's line, much more in fact than in the case of the ordinary spectrum. *The rays do not proceed directly from the surface of the liquid, but from a certain depth, those of short wave-lengths arising from deeper strata than those of greater length, so that the whole spectrum appears scalariform.* These phenomena cannot be observed if the spectrum is projected on the glass wall of the containing vessel instead of on the free surface of the liquid.

The author is unable to confirm the statements made by previous observers, that the thickness of the liquid layer or the concentration has any marked influence on the dispersion of the fluorescent spectrum; but he finds Stokes's law, that the refrangibility of the exciting is greater than that of the excited ray, to be strictly true.

T. C.

Molecular Rotatory Power of Carbon Compounds. By T. THOMSEN (*Ber.*, **14**, 203—206).—The author considers that the fact that the molecular rotation of a substance is influenced by the liquid in which it is dissolved is due to the chemical action of the solvent on the substance dissolved.

Thomsen's results are severely criticised by Landolt (*Ber.*, **14**, 296).

W. C. W.

Photo- and Thermo-electric Properties of Fluorspar. By W. HANKEL (*Ann. Phys. Chem.* [2], **11**, 269—278).—Many varieties of fluorspar when exposed to the action of light or to increase of temperature, develop electrical tensions on their surfaces. The middle of the faces under these circumstances becomes negative, the intensity gradually diminishing towards the angles and edges, and in some cases becomes positive there. The effects produced by light and by rise of temperature although similar in kind must be different in their origin, for on cooling the polarity becomes of the opposite sign, but after illumination the opposite polarities are not developed when the crystal is placed in the dark. Surfaces of cleavage become positive after exposure to light or to rise of temperature; this changes to negative as the temperature falls. Increase of temperature up to a certain limit (a little above 150°) favours the photo-electric sensibility of fluorspar.

T. C.

Electrolysis of Organic Substances in Aqueous Solutions. By HABERMANN (*Wien. Akad. Ber.* [2], **81**, 747—755).—The author's object was to find a method by which he could use either the nascent electrolytic oxygen or hydrogen respectively—during the continued action of the galvanic current—either for oxidation or reduction of organic substances in aqueous solutions.

He quotes from Wöhler, H. Kolbe (*Annalen*, **69**, 251), and Kekulé (*ibid.*, **131**, 79, 80, 81, 85) in support of the efficiency of his processes, which are as follows:—

For reductions, a Bunsen's electrolytic hydrogen apparatus is used, with the decomposition cell open at the top, and the platinum elec-

trode hung in a bell-shaped vessel, to the upper end of which the gas delivery tube is attached. The mouth of the bell dips under the liquid when in use; it is therefore tied over with a piece of linen to keep out the flocks of zinc hydrate, which would otherwise fall on the platinum electrode and interfere with the reaction.

For oxidations a similar arrangement is used, the platinum being the anode, whilst mercury covered to the depth of 1 centimeter with finely powdered red oxide of mercury forms the cathode.

D. A. L.

Chemical Energy and Electromotive Power of Various Galvanic Combinations. By J. THOMSEN (*Ann. Phys. Chem.* [2], 11, 246—269).—In order that the chemical energy of any galvanic combination may appear entirely as current electricity, no chemical action must occur when the circuit is open. From careful experiments detailed in the paper, the author concludes that in a closed Daniell's circuit the total chemical energy is converted into current electricity, and that the galvanic evolution of heat in the circuit is therefore equivalent to the chemical energy involved.

The chemical energy and electromotive power of various galvanic combinations have been compared, and it is found that a complete transformation of chemical energy into electricity takes place in Daniell's circuit, in Regnault's circuit (zinc—sulphuric acid—cadmium sulphate—cadmium), and in Pincus's circuit (zinc—hydrochloric acid—silver chloride—silver), *i.e.*, in those combinations in which the metallic surface of the negative electrodes undergoes no change during the electrolytic process. The same holds good approximately also in those combinations in which nitric acid is used (Bunsen's, zinc—sulphuric acid—nitric acid—carbon; and Thomsen's, copper—sulphuric acid—nitric acid—carbon, combinations), although the formation of reduction products slightly vitiates this result.

T. C.

Guthrie's Cryohydrates. By H. OFFER (*Wien. Akad. Ber.* [2], 81, 1058—1079).—According to the author, cryohydrates are simply mechanical mixtures of ice and salt. Definite crystals are not obtainable, but only opaque masses of crystalline structure, even if the cooling of the solution takes place very gradually; and from these masses alcohol dissolves out the ice, leaving a skeleton of the crystalline anhydrous salt. Cryohydrates, brought into cold water, do not simply dissolve, as might be expected were they chemical compounds, but become converted into transparent ice, free from salt.

Calorimetric determinations made upon cryohydrates of KNO_3 , KClO_3 , and K_2SO_4 , and upon ice of the same temperature, plus the uncombined salt in the same proportion as contained in the cryohydrate, furnished identical results.

The volume of the cryohydrates is equal to the sum of the volumes of their constituents.

Upon the basis of these results, the author denies the existence of cryohydrates as chemical compounds, and he is confirmed in his conclusion by the absence of any simple molecular proportions between the water and salt contained in them. Thus in the cryohydrate of NH_4Cl , 12.4 mols. of water, in that of KCl , 16.61, of Na_2CO_3 , 92.75, of

K_2SO_4 , 114.2, and of $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$, 165.6 mols. of water would be in combination with 1 mol. of salt.

The fact that the temperature remains constant during the separation of the cryohydrates affords no clue whatever as to the nature of the mass. Ice alone cannot separate from solutions cooled to the requisite temperature, as the remaining solution would be supersaturated for that temperature, whilst salt alone cannot crystallise unless the liquid become undercooled: hence salt and ice crystallise simultaneously in constant proportion at constant temperature.

O. H.

Thermic Properties of some Double Iodides. By M. BELLATI and R. ROMANESE (*Atti del R. Istituto veneto di scienze lettere ed arti* [5], 6).—The iodides studied by the authors were those originally obtained by Meusel, and by Willm and Caventou, on precipitating the double potassium and mercury iodide with silver nitrate and with a solution of copper sulphate in sulphurous acid respectively. In the first case, a yellow precipitate is thrown down, which has the property of becoming red when gently heated under water, whilst the scarlet copper salt changes to dark chocolate when heated to 70° , both salts recovering their original colour on cooling. As it seemed probable that the double salt prepared by Meusel's method might be a mixture, the authors investigated the reaction, and ascertained this to be the case: after many trials, they found that the best process for preparing the double iodide, $\text{HgI}_2(\text{AgI})_2$, was to mix the silver and mercuric iodides in the proportions indicated by the formula, and to grind the mixture in a mortar with alcohol until it had become canary yellow. Observations made on the rate of cooling of this compound, showed that there was a minimum velocity at about 43° . When gradually heated, the colour became darker, being orange at 47.5° , and orange-red at 48.5° , slowly taking a deeper shade as the temperature was raised. If allowed to cool from a temperature of 48.5° , the colour does not sensibly change until it falls below 43° .

Experiments were also made with the double copper salt, $\text{HgI}_2.\text{Cu}_2\text{I}_2$, prepared in a similar manner to the silver salt; here the minimum velocity in cooling was observed at 11° .

The densities of the compounds at 0° referred to water at 0° were determined: $\text{HgI}_2(\text{AgI})_2$ being 5.9984, and $\text{HgI}_2.\text{Cu}_2\text{I}_2$ 6.0956.

A detailed description of the dilatometer and the methods employed for the determination of the dilatation of the compounds $\text{HgI}_2(\text{AgI})_2$, $\text{HgI}_2(\text{AgI})_3$, and $\text{HgI}_2.\text{Cu}_2\text{I}_2$, is given. The dilatation of the silver salt, $\text{HgI}_2(\text{AgI})_2$, was found to be normal below 40° , being expressed by the formula

$$V_t = 1 + 0.0000953704t.$$

From 45 — 50° , it expands in an abnormal manner, plainly indicating a change of structure, whilst above 50° (to 80°) it again becomes normal

$$V_t = 1.006165 + 0.000088102t.$$

The curve representing these changes shows that the abnormal expansion commencing at about 42° is at first small, but goes on

gradually increasing until it attains a maximum at 49—51°, and then at 61·5° it passes abruptly to a small and perfectly normal expansion. These changes are analogous to those which take place in most solid bodies when undergoing fusion. On allowing the double salt to cool, a similar variation in the rate of expansion is observed, but here the abnormal period lies between 45° and about 30°. The salt, $\text{HgI}_2 \cdot (\text{AgI})_3$, behaves in a similar manner: below 40° its expansion is normal, the volume being represented by

$$V_t = 1.0000065689t;$$

from 40—50° it is abnormal, and above 50° it is again regular,

$$V_t = 1.003500 \text{ and } 0.000084005t.$$

The copper salt, $\text{HgI}_2 \cdot \text{Cu}_2\text{I}_2$, behaves normally below 62°, when

$$V_t = 1 + 0.000078460t;$$

from 63—72° it is abnormal, and above 72°

$$V_t = 1.006803 + 0.0000814728t.$$

The curve representing the abnormal dilatation of this compound shows that from 63—70° it increases slowly, but very rapidly between 70° and 71°, the expansion becoming regular again at 71·3°. On cooling, the maximum change in the rate of expansion occurs at about 60°.

The specific heat of the compound $\text{HgI}_2(\text{AgI})_2$ for any temperature T below 41° is expressed by the formula—

$$C = 0.035648 + 0.0011567T - 0.0000157863T^2;$$

the heat necessary to raise the unit of weight of the compound from 0° to T° , with modification of structure, is

$$Q_{0-T} = 1.58600 \text{ and } 0.0613035T,$$

whilst the specific heat of the compound above 51° is constant, and equal to 0.06130.

The *heat of transformation* is the amount of heat absorbed (λ) or evolved (λ_1) by the unit of weight of the compound in passing from the one state to the other, supposing the temperature to remain constant. If the temperature is raised, and the change of state is supposed to occur suddenly and completely at 50°, then $\lambda = 2.0807$; but if the temperature is supposed to fall and the change to occur at 41°, then $\lambda_1 = 2.0283$. The amount of heat λ is sufficient to raise the temperature of the compound 38°, and is therefore relatively greater than the heat of fusion of some substances.

For the compound $\text{HgI}_2(\text{AgI})_3$:—

$$C = 0.054404 + 0.000159362T, \text{ and}$$

$$Q_{0-T} = 1.46850 + 0.0641046T$$

$$\lambda = 1.7525 \text{ and } \lambda_1 = 1.7323.$$

For the compound $\text{HgI}_2 \cdot \text{CuI}_2$:—

$$C = 0.0532068 + 0.000082262T, \text{ and}$$

$$Q_{0-T} = 1.90297 + 0.0626421T$$

$$\lambda = 2.3619 \text{ and } \lambda_1 = 2.3210.$$

C. E. G.

Thermochemistry of the Bromides and Iodides of Phosphorus. By J. OGIER (*Compt. rend.*, **92**, 83—86).—The heats of combination determined by the author are as follows :—

P sol. + I ₂ gas	= PI ₂ sol.	disengage 20·6 heat-units.
P „ + I ₃ „	= PI ₃ „	„ 27·1 „
P „ + Br ₃ „	= PBr ₃ sol.	„ 83·0 „
PBr ₃ + Br ₂ „	= PBr ₅ „	„ 28·4 „

R. R.

Thermochemistry of Certain Haloïd Salts. By BERTHELOT (*Compt. rend.*, **91**, 1024—1030).—The property possessed by many metallic chlorides of forming definite compounds with hydracids is more general than has hitherto been supposed, and as these compounds play an essential part in many reactions, the author has resumed his study of them, from both the chemical and thermic points of view. The researches detailed in the papers relate to the haloïd salts of cadmium, lead, silver, and mercury.

R. R.

Magnetic Oxide of Iron. By BERTHELOT (*Compt. rend.*, **92**, 17—22).—The researches detailed in this paper show that in the reaction $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$, the quantity of heat disengaged is 4·4 heat-units. The determinations were made on a variety of magnetic oxide of iron easily attacked by acids.

R. R.

Heat of Combustion of Carbon Compounds. By J. THOMSEN (*Ber.*, **13**, 2320—2324).—According to the author, the theoretical conclusions of Quesneville (*Moniteur Scientifique*, November, 1880) on the heat of combustion of carbon compounds are valueless, as they are deduced from incorrect observations.

W. C. W.

Vapour-density of Chlorine. By V. MEYER (*Ber.*, **13**, 1721—1723).—The vapour-density of chlorine from platinous chloride, as given by C. Meyer and the author (this Journal, **38**, 214), is too low, owing to some undiscovered source of error. A re-determination at temperatures similar to that used in the case of iodine (this Journal, **38**, 788), gave a result 2·05, intermediate between the normal density and the result obtained before (*loc. cit.*). This the author regards as showing that by a further increase of temperature, a further decrease in density will be observed. As regards the source of error pointed out by Peterson and Ekstrand (this Journal, **38**, 841), the author shows the air condensed by platinous chloride to be too small to affect the result. Further, the recent determinations of the density of iodine vapour at 1250° by Troost (*Compt. rend.*, **91**, 55), proved that the results obtained by Dumas' method agree with those obtained by the author's method.

P. P. B.

Volume Relations in the Formation and Decomposition of Salts. By W. MÜLLER-ERZBACH (*Ber.*, **14**, 217—222).—An examination of a large number of metallic carbonates, sulphates, and nitrates shows that whenever an act of double decomposition is attended by an evolution of heat, it is also accompanied by a contraction of the total volume of the bodies taking part in the reaction.

W. C. W.

Specific Volumes of Oxides. By B. BRAUNER and J. I. WATTS (*Phil. Mag.* [5], **11**, 60—64).—The specific volumes of all the normal

oxides at present known are arranged in a table which is of the same form as Mendelejeff's original classification of the elements (*Annalen, Sup.*, 8, 143). The numbers refer to one atom of the metal in the form of oxide. Such a table shows that the specific volume increases in each horizontal series from left to right, and also with the atomic weight in each vertical group, and further that there is a characteristic difference between the members of the odd and even series of the table. The specific volume of any oxide may be found from a consideration of the surrounding values.

If the volume which one atom of oxygen possesses in the various oxides be found by subtracting the specific volume of the metal (which is supposed to enter into combination without alteration) from that of the oxide, it is seen:—(1.) In strong bases the oxygen has a negative value. (2.) In the oxides of heavy metals and metalloids the volume of the oxygen is positive. (3.) The earth metals unite with oxygen without any appreciable change of volume, and thus form a connecting link between acids and bases. (4.) The higher the specific volume of the element in the oxide, the less positive or more negative is the specific volume of the oxygen. (5.) The more negative the value of the oxygen, the greater is the affinity of the metal for the oxygen.

The following specific gravity determinations are new:— Li_2O at $15^\circ \text{C.} = 2.102$, sp. vol. = 7.12 ; Bi_2O_3 at $2^\circ = 5.918$; UO_3 at $2^\circ = 5.26$, and 5.02 .
T. C.

Volume Constitution of Liquid Compounds. By H. SCHRÖDER (*Ann. Phys. Chem.* [5], 11, 997—1015).—The boiling points and molecular volumes of a number of compounds are compared, and it is shown:—(1.) That in many series of isomeric compounds, those isomerides which have the highest boiling point have also the greatest molecular volume. This holds good in the case of the acids and their isomeric ethers, of the normal and their isomeric iso-compounds, and of the isomeric ethers themselves. (2.) That in many series of compounds the differences of boiling point diminish, whilst the differences of molecular volume increase as the atomic weight increases. This is applied in the case of the halogen compounds of phosphorus, antimony, and the alcohol radicals, and also in the case of certain acids, ethers, alcohols, &c.

In conclusion, the author discusses the bearing of his theory of steres on these facts, and concludes that the volumes occupied by the elements of any compound stand to one another in simple proportions, and that carbon, hydrogen, oxygen, and nitrogen each generally occupy one stere. In certain cases, however, these elements have a different condensation or stere-value depending on the quantivalence which they exhibit in the compound.
T. C.

NOTE.—It has already been pointed out by Carnelley (*Proc. Roy. Soc.*, 197, 1879; *Phil. Mag.*, Nov., 1879, 368) that in many series of compounds, both organic and inorganic, the difference of boiling point and also of melting point diminishes as the atomic weight increases.

Inorganic Chemistry.

Density of Iodine Vapour. By J. M. CRAFTS and F. MEIER (*Compt. rend.*, **92**, 39—42).—The authors have investigated the anomalous decrease of the density of iodine vapour attending rise of temperature, which was discovered by Meyer. Their results show that at a temperature below 700° the density is normal, and corresponds with the molecular constitution I_2 ; that between 700° and 1400° it gradually decreases as the temperature rises; after the higher limit is reached, it again becomes constant with half its former value, thus indicating the molecular condition represented by I . The exact limits of temperature and the curves representing the change vary with the tension.
R. R.

Preparation of Ozone by Heating Substances containing Oxygen. By A. R. LEEDS (*Ber.*, **13**, 2351—2353).—The so-called ozone reaction exhibited by the oxygen evolved by the action of heat on mercury and silver monoxides, manganese and lead di-oxides, and periodic acid, is due to traces of chlorine contained in the oxides.
W. C. W.

Nitrification. By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **91**, 134—136).—In a mixture of oxygen and nitrogen, the silent electrical discharge taken at very low tensions does not determine the formation of any appreciable quantity of ozone. The spectroscope, however, indicates the existence in the mixture of a compound of oxygen and nitrogen, and when the gases are made to pass through a heated tube, the decomposition of this compound is shown by the spectrum of hyponitrous acid making its appearance. The results of the authors' observations and those of Berthelot show that a spark or powerful silent discharge produces pernitric acid, which, by the attendant elevation of temperature, is converted into hyponitrous acid. It follows, therefore, that silent discharges, corresponding with feeble tensions, are able to furnish nitric acid as the ultimate result of the decomposition of pernitric acid.
R. R.

Spectra of Compound Gases and a New Compound of Nitrogen and Oxygen. By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **92**, 80—83).—The absorption-bands of ozone prepared from pure oxygen, disappear slowly at ordinary temperatures, rapidly when the gas is exposed to a red heat. The same results are obtained when the ozone is mixed with nitrogen, without the latter having traversed the electrical apparatus; that is, the heat does not determine the formation of hyponitric acid. Chemists are agreed that by the silent electric discharge, ozone may be prepared in the presence of nitrogen, if only weak electric tensions are employed. The authors have found that when the silent discharge is passed through a dry mixture of oxygen with at least one-seventh of nitrogen at the ordinary temperature, a substance hitherto unobserved is formed, its

presence being indicated by a very remarkable absorption-spectrum characterised by fine very dark lines in the red, orange, and green. Electrified nitrous, or hyponitrous, or anhydrous nitric acid does not yield this spectrum. Water or a trace of moisture immediately causes the spectrum to disappear, and the substance is therefore an anhydrous compound capable of forming an acid. The mixture of ozone and the new substance is changed by a red heat, yielding hyponitrous acid. At ordinary temperatures, the change is slow, and a period of from 24 to 48 hours occurs after the disappearance of the dark lines of the new substance, before those of the hyponitrous acid make their appearance. The authors confirm an unpublished observation of Berthelot, namely, that a mixture of hyponitrous acid and oxygen was rendered colourless by the silent discharge, and they found the colourless mixture to yield the spectrum of the new substance, but none of the bands of hyponitrous acid. These results can be explained by admitting the formation of a *pernitric acid* formed under conditions analogous to those under which Berthelot found persulphuric acid to be produced.

R. R.

New Derivative of Nitrogen Sulphide. By E. DEMARÇAY (*Compt. rend.*, **91**, 1066—1068).—Among the products of the reaction of nitrogen sulphide on yellow chloride of sulphur is a substance forming yellow microscopic crystals soluble in water. These are regarded by the author as the chloride of a radical, S_4N_3 , which he proposes to designate *thiotritiazyle*, and of which he describes a nitrate and a bisulphate. The former crystallises in large lemon-yellow plates, and the latter in pale-yellow needles.

R. R.

Action of Phosphorus on Hydriodic and Hydrobromic Acids. By A. DAMOISEAU (*Bull. Soc. Chim.* [2], **35**, 49—51).—When a current of hydriodic acid gas is passed over yellow phosphorus at ordinary temperatures, phosphonium iodide and phosphorus diiodide are formed, and a small quantity of the phosphorus is converted into the red modification, $P_5 + 8HI = 2PH_4I + 3PI_2$. When the same gas is passed over red phosphorus no reaction takes place, even if the latter be heated to 100° . A trace of phosphonium iodide is formed, but its formation is probably due to the presence of a small quantity of ordinary phosphorus.

If the phosphorus is added to a concentrated solution of hydriodic acid at ordinary temperatures, the same reaction takes place, although somewhat less rapidly. The phosphonium iodide and phosphorus diiodide produced are not decomposed so long as the hydriodic acid is in excess. If the phosphorus is added in excess, the reaction is modified by the presence of the water. The phosphorus diiodide is decomposed with production of phosphorus acid and hydriodic acid; the latter acts on a fresh quantity of phosphorus, forming phosphonium iodide and phosphorus diiodide; this latter is at once decomposed, and thus the final products of the reaction are phosphonium iodide and phosphorus acid, $P_2 + HI + 3H_2O = PH_4I + H_3PO_3$. But saturated solutions of hydriodic acid contain about $3\frac{1}{2}$ mols. of water to 1 mol. of acid; consequently, during the progress of the reaction, the relative

proportion of water present rapidly increases and the reaction is limited by the decomposition of the phosphonium iodide. The series of reactions ends in a state of equilibrium between the reacting bodies and the products formed. If gaseous hydriodic acid be passed into the liquid, or a small quantity of iodine and phosphorus be introduced, the formation of phosphonium iodide recommences, and the whole liquid is quickly converted into a mass of crystals of phosphonium iodide and phosphorous acid.

To prepare phosphonium iodide by means of this reaction, 10 parts of white phosphorus in small pieces are added to 22 parts of a cold saturated solution of hydriodic acid. After some hours 2 parts of iodine are added, the mass of crystals which forms is freed from phosphorous acid by washing with a solution of hydriodic acid, and the phosphonium iodide is dried as quickly as possible. It contains traces of phosphorus iodide and red phosphorus, but is sufficiently pure for most purposes. Hydriodic acid solution acts slowly on red phosphorus at ordinary temperatures; after some hours crystals of phosphonium iodide are formed.

Hydrobromic acid solution does not act on phosphorus in the cold. In sealed tubes at 100–120° phosphonium bromide is formed in considerable quantity. In no case was phosphorus bromide obtained, and the author has found that phosphorus tribromide is gradually decomposed by a concentrated solution of hydrobromic acid. C. H. B.

Fluo-salts of Tellurium. By A. HÖGBOM (*Bull. Soc. Chem.* [2], 35, 60–62).—Solutions of tellurous acid and various hydrates and carbonates in hydrofluoric acid, were evaporated over oil of vitriol. No salts were obtained with glucinum, silver, copper, or nickel. The solutions of copper and nickel gave well formed-crystals of the simple fluorides. When the tellurium fluoride was in excess, crystals were obtained having the composition $\text{TeFl}_4 \cdot 4\text{H}_2\text{O}$. Potassium, barium, and ammonium gave salts having the general formula RTeFl_5 . These double salts crystallise somewhat easily, but the crystals become opaque when exposed to the air, and are apparently decomposed by water. The ammonium salt, $\text{NH}_4\text{TeFl}_5 \cdot \text{H}_2\text{O}$, crystallises in colourless prisms; the potassium salt, KTeFl_5 , in long colourless needles; and the barium compound, $\text{BaTe}_2\text{Fl}_{10} \cdot \text{H}_2\text{O}$, in irregular lamellæ.

C. H. B.

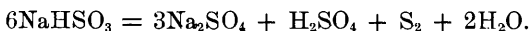
Action of Hydrochloric Acid on Metallic Chlorides. By A. DITTE (*Compt. rend.*, 91, 986–989).—In this paper, the solubility of mercurous chloride in hydrochloric acid is traced to the formation of a crystallisable compound, $\text{Hg}_2\text{Cl}_2 \cdot \text{H}_2\text{Cl}_2$; and the author considers that analogous compounds are formed in the cases of the chlorides of gold, platinum, bismuth, and antimony. On the other hand there exists a class of chlorides represented by AgCl , the solubility of which is but slightly increased by hydrochloric acid, and on cooling the solutions nothing but the anhydrous chloride separates. R. R.

Solubility of a Mixture of Sodium and Potassium Chlorides. By J. SCHÖNACH (*Wien. Akad. Ber.* [2], 80, 525–533).—The author finds that when sodium and potassium chlorides are together

dissolved in water, so that the solution is saturated for both salts, the solubility of both salts is diminished, that of potassium chloride in a greater degree than sodium chloride. The solubility of the mixture does not correspond to the sum of the solubilities of the two salts, but is less the higher the temperature. The less soluble salt is removed by the more soluble salt, in accordance with the law of Hauer.

O. H.

Action of Heat on Sodium Hydrogen Sulphite. By G. A. BARBAGLIA and P. GUCCI (*Ber.*, **13**, 2325—2326).—When a concentrated solution of sodium hydrogen sulphite is heated in sealed tubes at 150°, it is decomposed into sulphate, sulphur, and free sulphuric acid—



Solutions of the acid sulphites of magnesium and of ammonium undergo similar decomposition.

W. C. W.

Sodium Borotungstates. By D. KLEIN (*Compt. rend.*, **91**, 1070).—Continuing his researches on the products of the reactions he has already described (this Journal, 1880, *Abstr.*), the author in the present paper details the preparation of disodic and tetrasodic borodecitungstates.

R. R.

Atomic Weight of Glucinum. By B. BRAUNER (*Phil. Mag.* [5], **11**, 65—71).—Nilson and Pettersson (*Wiedemann's Ann. Chem.*, **4**, 554; *Ber.*, **11**, 381, 906; **13**, 2035) have recently proposed the view that glucinum is trivalent, and not bivalent, as hitherto supposed. This they contend is supported (1) by the specific heat of the element, and (2) by a comparison of the molecular volumes and molecular heats of the rare earths and their sulphates. The first of these has been discussed by L. Meyer (*Ber.*, **13**, 1780), and it is therefore only the latter which is dealt with in the present communication. The author concludes that the molecular volume of glucinum, the molecular volume of the sulphate, the molecular heat of the oxide, the atomic heat of the oxygen contained in it, and the chemical nature of the metal itself, all require that the element should be bivalent, and have the atomic weight 9.1. The physical constants for the oxide GO correspond exactly with the dyad position usually assigned to glucinum in the periodic classification, which position is completely analogous to that of the element lithium, so far as the physical properties of this metal are known. Finally the authors give a new confirmation of the view that glucinum, like eleven other elements of low atomic weight and small atomic volume, is an exception to the law of Dulong and Petit.

T. C.

Distribution of the Cerite Metals. By A. COSSA (*Gazzetta*, **10**, 465—466).—In a former paper (this Journal, *Abstr.*, 1879, 695) the author pointed out that cerium, lanthanum, and didymium were very widely distributed, being found not only in numerous rocks, but also in bones, and in the ashes of rice, tobacco, and the beech; he has since found them in the ashes of other plants, notably the vine. It seemed a matter of importance to ascertain if they were present also in the

human body, and it was found in an experiment on 600 kilograms of urine, that the pure oxalates of the cerium metals could be isolated in quantity sufficient to give the characteristic reactions of these metals.

In the former paper, it was stated that these metals were associated with calcium in preference to magnesium, and an examination of 50 grams of wagnerite failed to show any trace of the metals, whilst the same quantity of apatite gives abundant indications. Kjerulfina, from Bamle, which is wagnerite more or less converted pseudomorphically into apatite, was examined; on separating the two minerals, the apatite was found to contain the cerium metals, whilst the wagnerite was quite free from them.

C. E. G.

Didymium Tungstate. By A. COSSA (*Gazzetta*, 10, 467—468).—The crystallographic determinations of Sella having shown that artificial didymium tungstate (this Journal, 1879, Abstr., 695) is isomorphous with scheelite, the author was induced to undertake experiments to ascertain if its molecular specific heat is conformable with the hypothesis of the bivalence of didymium in the neutral tungstate. The didymium tungstate was prepared in a manner similar to the cerium compound, by adding a solution of didymium sulphate to one of normal sodium tungstate. The washed and calcined precipitate is amorphous, and fuses more readily than the cerium compound, or than scheelite, yielding a homogeneous, rose-coloured, crystalline mass. Its specific gravity at 14° is 6·69, and the mean of 11 determinations of its specific heat by Kopp's method was 0·0831. This multiplied by the molecular weight of $\text{DiWO}_4 = 344$ gives 28·58, a number agreeing closely with the theoretical for the normal tungstate of a bivalent radical, and with that found for cerium tungstate (27·21), and for scheelite (28·94). This in conjunction with the crystallographic observations, tends to show that didymium in didymium tungstate is bivalent.

C. E. G.

Action of Hydrofluoric Acid on Ammonium Dichromate. By L. VARENNE (*Compt. rend.*, 91, 989).—Ammonium dichromate treated with excess of hydrofluoric acid yields shining bright red crystals of a substance having the composition—



When exposed to air, these crystals change but slowly; they attack glass, are immediately decomposed by heat, disengaging a gas which acts on glass. The edges of the platinum vessel in which the mixture of hydrofluoric acid and ammonium dichromate was boiled were found to have been acted on by a gas which escaped in extremely small bubbles, at the same time that a peculiar odour was noticed. The author's suggestion is that possibly fluorine was liberated.

R. R.

Chromium Sulphides. By M. GRÖGER (*Wien. Akad. Ber.* [2], 81, 531—538).—The author has succeeded in preparing several double sulphides of chromium and zinc, iron, &c., corresponding to the double oxides of chromium and the same metals.

Trichromic tetrasulphide, Cr_3S_4 , is prepared by heating dried chro-

mium oxide with an excess of finely powdered sulphur in a current of hydrogen in a Rose's crucible, until no more sulphur is volatilised. It is advisable after cooling to remix the product with sulphur and repeat the operation. The sulphide, which corresponds with magnetic iron oxide, Fe_3O_4 , is a greyish-black powder, insoluble in water, very slightly soluble in concentrated hydrochloric acid, but easily soluble in strong nitric acid.

Zinc sulphochromite, ZnCr_2S_4 , is obtained by heating a mixture of zinc and chromium hydroxides with sulphur. The mixture is prepared by precipitating with ammonia solutions of zinc and chromium sulphates mixed in the proportion of rather more than 1 mol. of ZnSO_4 to 1 mol. of CrSO_4 . The heating is commenced in a Rose's crucible; then the substance is finely powdered and heated in porcelain boats in sulphur vapour for four hours, and afterwards in a current of carbonic anhydride until no more sulphur is given off. The product is finally boiled with concentrated hydrochloric acid. It is a dark brown powder, which is insoluble in water, almost insoluble in concentrated hydrochloric acid, but soluble in nitric acid and in *aqua regia*.

Ferrosulphochromite, FeCr_2S_4 , is prepared from a mixture of iron and chromium hydroxides in a manner similar to the zinc compound. It is a black powder, insoluble in water and concentrated hydrochloric acid, but soluble in nitric acid and in *aqua regia*.

Manganese sulphochromite, MnCr_2S_4 , prepared in a manner similar to the two preceding compounds, is a chocolate-brown powder, which is insoluble in water and strong hydrochloric acid, but soluble in nitric acid and *aqua regia*.

The compound Cr_2S_3 appears to play the part of the sulphanhydride of the hypothetical acid $\text{H}_2\text{Cr}_2\text{S}_4$.

J. I. W.

Separation of the Metals of Platinum Ores. By E. WILLM (*Bull. Soc. Chim.* [2], **34**, 679).—The ore is dissolved in *aqua regia*, the greater part of the platinum separated by means of ammonium chloride, and the other metals precipitated by zinc. The precipitate is treated with nitric acid, and the neutral solution of the nitrates agitated with mercury, when the palladium is precipitated, together with other metals of the platinum group.

C. H. B.

Platinous Hypophosphite. By R. ENGEL (*Compt. rend.*, **91**, 1068—1070).—The author obtained platinous hypophosphite by passing a current of phosphoretted hydrogen into an aqueous solution of platinum tetrachloride. It is a yellow powder, insoluble in water, alcohol, or acids. Placed in suspension in solutions of gold, silver, copper, mercury, or palladium, it immediately reduces the salts even in the cold, and at the same time is itself partially reduced.

R. R.

Mineralogical Chemistry.

Formation of Hydrogen in the Stassfurt Potash Mines. By H. PRECHT (*Ber.*, **13**, 2326—2328).—The hypothesis that the hydrogen in the Stassfurt carnallite beds owes its origin to the decomposition of water by ferrous chloride, is supported by the discovery of the occurrence of a ferrous potassium chloride, $\text{FeCl}_2 \cdot 2\text{KCl} + 2\text{H}_2\text{O}$, in these deposits. The mineral, to which the name "Douglasite" has been given, is found in small crystals, of a green colour.

W. C. W.

Contemporaneous Production of Native Sulphur in the Subsoil of Paris. By DAUBRÉE (*Compt. rend.*, **92**, 101—103).—The paper describes the occurrence of native crystallised sulphur in the subsoil of Paris. It has its origin in the action of organic matters on calcium sulphate. The author is of opinion that the deposits of sulphur found in stratified rocks have a similar origin.

R. R.

Covellin occurring as encrusting Pseudomorph on a Bronze Celtic Axe found on the Salzberg near Hallstadt. By F. v. HOCHSTETTER (*Jahrb. f. Min.*, 1880, **1**, Ref. 42)*.—In an old timbering discovered at the above-mentioned locality in 1877, and doubtless coeval with the well known Celtic tombs occurring there, there were found embedded in a very fine and tenacious blue clay a so-called "Palstab," of bronze, and a lump of metallic copper of the size of a hen's egg, both of which were coated with a blue crust from 0.5 to 1 cm. thick.

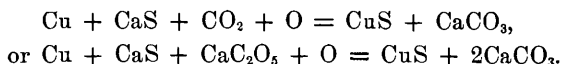
The analysis of the crust on the last-mentioned object, in which small beads of copper pyrites could be recognised, gave 33.37 p. c. sulphur and 66.26 copper, which, together with the density (4.611), the colour, the shining streak, and the mild texture, shows that the encrusted substance consists of covellin, CuS .

A cross section of the object showed that only the external zone consists of pure compact covellin, while the inner layer of this crust has a scaly structure, and is mixed with copper pyrites; and beneath this comes a layer having a decided tinge of grey, and resolvable in thin section under the microscope into covellin and metallic copper, mixed with larger and smaller granules of calcium carbonate. Close upon the upper nucleus, which is much corroded and jagged with hollows and teeth, lie also spherules of calcium carbonate 2 mm. in diameter, which from their crystalline aspect are regarded by the author as arragonite.

The formation of this encrusting pseudomorph is easily explained by the nature of the locality. Gypsiferous clay containing large quantities of animal and vegetable remains yielded a plentiful supply of calcium sulphide and hydrogen sulphide; and these compounds either acted directly on the copper, or if, as Bonsdorff supposes, they acted on it only after it had been attacked by moist air containing

* The *Jahrbuch für Mineralogie* is now published in two volumes annually, each containing Original Memoirs and Abstracts (Referate) separately paged.

carbonic acid, the carbonic acid in this instance playing an active part; then the copper must have been precipitated at the moment of formation of the carbonate. The process may be represented by the following equations:—



The copper pyrites may be supposed to have been formed when the ferrous solution was neutralised, whereupon also iron sulphide was precipitated and entered into combination with the copper sulphide.

A similar product from the same locality was described in 1872 by Priwoznik (this Journal, 25, 882).

Lastly, the author notices various pseudomorphoses of the sulphides of iron and copper and of the compounds of cupric oxide, and points out that native copper under ordinary circumstances can be converted only into cupric compounds, no instance having yet been observed of the pseudomorphosis of a sulphide of copper after metallic copper.

H. W.

A New Form of Tetrahedrite. By F. W. CLARKE and MARY E. OWENS (*Ber.*, 13, 1786—1787).—A specimen of a mineral from Arizona is described. It was massive, of a steel-grey colour, sp. gr. 4.34—4.36, and possessing all the properties of a tetrahedrite. The results of analysis are as follows:—

S = 21.67 p. c.	Cu = 33.53 p. c.	Ag = 1.80 p. c.
Sb = 24.72 „	Pb = 16.23 „	Fe = 0.56 „

This mineral does not correspond with any described species, and its atom-relations point to its being a tetrahedrite in which part of the copper is replaced by lead.

V. H. V.

Nickel-speiss (Placodin). By J. BRAUN (*Jahrb. f. Min.*, 1880, 1, Ref. 46).—The nickel-speiss described by Gustav Rose as quadratic was regarded by Breithaupt as monoclinic, and designated as *placodin*. Braun, however, finds that, in spite of the similarity of habit which the crystals exhibit to Breithaupt's placodin, their faces are nevertheless reducible to the quadratic forms described by Rose, and that the apparently monoclinic character of the crystals is due to peculiarities of development. Axial ratio $a : c = 1 : 1.125$. Besides the forms observed by Rose and Breithaupt, viz., P, 2P, $\frac{2}{3}$ P, $\frac{4}{3}$ P, and 0P, Braun has distinguished the following: $\frac{4}{5}$ P, $\frac{1}{12}$ P, $\frac{8}{7}$ P.

The formula Ni_2As , given by Breithaupt, has not been confirmed by the numerous analyses made by others, whose results moreover differ considerably from one another. Braun endeavours to account for this diversity of composition by regarding nickel-speiss as a mixture or alloy, the forms of which are not altered by the addition of small proportions of foreign substances. A new analysis made with a small quantity of substance gave 55.56 p. c. Ni(Co), 37.50 As, and 5.76 S, whence may be deduced the atomic proportion $\text{Ni}_{38}\text{As}_{20}(\text{S}_2)$, indicating that the substance analysed may be regarded as essentially Ni_3As_2 . Sp. gr. = 7.694.

H. W.

Two New Mineral Species from the Mineral Locality of Fairfield Co., Connecticut. By G. J. BRUSH and E. S. DANA (*Sill. Amer. Jour.*, 1879, vol. 7).—1. *Fairfieldite*.—This mineral occurs in crystalline groups, rarely in distinct crystals. Many laminar alterations of it are similar in structure to gypsum, while others are more cauliform and resemble stilbite. Hardness = 3·5; sp. gr. = 3·15; cleavage perfect parallel to $\infty P\infty$; less distinct parallel to $\infty P\infty$. The lustre is inferior to that of diamond, and resembles that of mother-of-pearl; very bright on the cleavage-surface. The mineral is transparent, and has a white to yellowish colour. Two distinct varieties have been found, one (A) filling cavities in reddingite (this Journal, 1879, 36, 892) and coating the crystals of that mineral, the other occurring more abundantly and penetrated by quartz. *Fairfieldite* is also found in small quantities accompanying eosphorite, triploidite, and dickinsonite (*ibid.*, 20 and 891).

The crystals, rarely well defined, are triclinic. Axes, $a : b : c = 0.2797 : 1 : 0.1976$. Axial angles, $\alpha = 120^\circ 9'$; $\beta = 94^\circ 33'$; $\gamma = 77^\circ 20'$. Observed forms, $0P$, $\infty P\infty$, $\infty P\infty$, P' , $\frac{1}{2}P'$, $\frac{1}{3}P'$, $4P'4$, $\infty P'\frac{3}{2}$, $\infty P'$, $\infty P'\frac{3}{2}$, $\infty P'2$, $\infty P'$. Fundamental angles, $\infty P\infty : 0P = 92^\circ$; $\infty P\infty : \infty P\infty = 78^\circ$; $\infty P\infty : P' = 123^\circ 30'$; $0P : P' = 147^\circ$; $\infty P\infty : P' = 101^\circ 30'$.

The mineral heated in a closed tube gives off water without acid or alkaline reaction, and at the same time becomes yellow, brown, and finally magnetic. It colours flame pale-green; dissolves in hydrochloric and in nitric acid. Chemical analysis, by H. Penfield, gave for the two varieties the following values, leading to the formula $R_3P_2O_8 + 2aq$.

	P_2O_5 .	FeO.	MnO.	CaO.	Na_2O .	K_2O .	H_2O .	Quartz.
A ..	38.39	5.62	15.55	28.85	0.73	0.13	9.98	1.31 = 100.56
B ..	39.62	7.00	12.40	30.76	0.30	—	9.67	0.55 = 100.30
Calc.	39.30	6.64	13.10	30.99	—	—	9.97	— = 100

The proportions of the metallic constituents are $Ca : Mn + Fe = 2 : 1$ and $Mn : Fe = 2 : 1$. The analyses show that the two varieties do not differ much one from the other.

2. *Fallowite* occurs in crystallo-granular masses, rarely in distinct crystals. Among the accompanying minerals are triploidite, *fairfieldite*, and *reddingite*; the last is especially difficult to distinguish from *fallowite*. Hardness = 4·5; sp. gr. = 3·41—3·45. Lustre resinous and fatty. Colour mostly wax-yellow, seldom colourless. Transparent to translucent. Fracture uneven. Brittle. Cleavage perfect parallel to $0P$. The crystals have a rhombohedral aspect, but are nevertheless monoclinic and optically biaxial. Axes, $a : b : c = 1.7303 : 1 : 1.4190$; $\beta = 89^\circ 51'$. Observed forms, $0P$, $-2P\infty$, $+P$. Fundamental angles, $0P : +P = 121^\circ 20'$; $0P : -2P\infty = 121^\circ 29'$; $+P : -P = 84^\circ 37'$. Chemical analysis, by H. Penfield, gave in two determinations values agreeing nearly with the formula $3R_3P_2O_8 + H_2O$, in which R denotes $Mn : Fe : Ca : Na_2 = 6 : 1 : 1 : 1$.

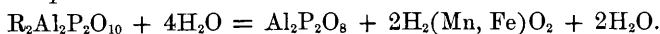
	P ₂ O ₅ .	FeO.	MnO.	CaO.	Na ₂ O.	Li ₂ O.	H ₂ O.	Quartz.
I.	39·06	9·48	39·48	not det.	5·65	0·07	1·75	0·86
II.	39·15	9·18	39·36	4·08	5·84	0·04	1·56	0·90 = 100·11
Calc.	40·19	6·80	40·19	5·28	5·84	—	1·70	— = 100

The water, though small in quantity, must be regarded as essential, inasmuch as all crystals of the mineral, even the most transparent, give off water when heated.

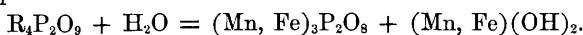
Reddingite, previously examined by the authors, as already observed (p. 229), has been shown to be completely homœomorphous with scorodite and strengite, whereas the composition of these minerals is as follows: *scorodite*, Fe₂As₂O₈ + 4aq; *strengite*, Fe₂P₂O₈ + 4aq; *reddingite*, Mn₂P₂O₈ + 3aq. Reddingite therefore contains monoxide instead of sesquioxide, and only 3 mols. water instead of 4. These results have been confirmed by a new analysis made by H. Wells.

The following is a comparative view of the composition and crystal-line forms of the new minerals found at Fairfield:—

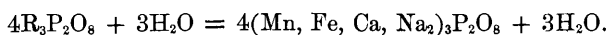
1. *Eosphorite*. Rhombic—



2. *Triploidite*. Monoclinic—



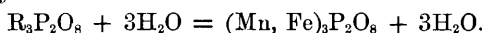
3. *Dickinsonite*. Monoclinic—



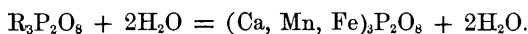
4. *Lithiophyllite*. Rhombic—



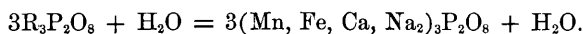
5. *Reddingite*. Rhombic—



6. *Fairfieldite*. Triclinic—



7. *Fillowite*. Monoclinic—

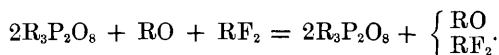


H. W.

Composition of Kjerulfin. By C. RAMMELSBURG (*Jahrb. f. Min.*, 1879, 1, Ref. 24).—A new analysis of homogeneous kjerulfin, which was merely intergrown with a small quantity of rutile, yielded

F.	P ₂ O ₅ .	MgO.	CaO.	Loss by ignition.
6·23	44·23	44·47	6·60	0·77 = 102·30.

Consequently F : P : R = 1·05 : 2 : 3·95 or 1 : 2 : 4, agreeing with the formula



In wagnerite, according to the author's analyses, the ratio F : P : R

= 1 : 1 : 2, leading to the formula $R_2P_2O_6 + RF_2$ ($R = Mg, Ca, Fe$). Moreover, the specific gravities of the two minerals are

Wagnerite.	Kjerulfin.
3.13 Fuchs.	3.15 v. Kobell.
3.068 Rammelsberg.	3.14 Rammelsberg.

The two minerals appear also to agree in cleavage and crystalline form; the hardness of wagnerite, however, is greater than that of kjerulfin, independently of pseudomorphs containing 94 per cent. silica. Wagnerite and kjerulfin may therefore be regarded as qualitatively similar but quantitatively different.

On the examination of kjerulfin by Pisani, who regards it as identical with wagnerite, and shows that many kjerulfins are partly converted into apatite, see this Journal (1879, **35**, 441). H. W.

Mineralogical Contributions. By G. VOM RATH (*Jahrb. f. Min.*, 1880, **1**, Ref. 38).—1. *Hannayite*.—This mineral, discovered by H. Mac-Ivor in the guano of the Skipton caves near Ballarat (Victoria), forms triclinic crystals, having the axial ratio $a : b : c = 0.69903 : 1 : 0.97432$ and the axial angles (in the front right upper octant), $\alpha = 122^\circ 31'$; $\beta = 126^\circ 46'$; $\gamma = 54^\circ 10\frac{1}{2}'$. Angles of co-ordinate planes: $A = 106^\circ 45\frac{1}{2}'$; $B = 114^\circ 32'$; $C = 67^\circ 2'$. Observed forms: $\infty P'$, $\infty' P$, $P\bar{3}$, $\infty P\bar{\infty}$, $0P$. Habit, prismatic in the direction of $\infty P'$ and $\infty' P$. Cleavage parallel to these same faces, also to $P\bar{3}$ and a prism $\infty P\bar{3}$. Sp. gr. = 1.893. Colour light brown. The crystals do not undergo any alteration at 100° , but when heated to 100 — 115° they become opaque and lose 21.08 per cent. in weight. Analysis gave

P_2O_5 .	MgO.	$(NH_4)_2O$.	H_2O .
I. 45.63	18.72	8.19	23.12 = 100.66
II. 45.77	19.08	7.99	28.29 = 101.13

If about 28 per cent. of the water be regarded as constitutional, these numbers lead to the formula $(NH_4)_2O, 2H_2O, 3MgO, 2P_2O_5 + 8aq$, or $(NH_4)_2H_4Mg_3(PO_4)_4 + 8aq$.

2. *Newberyite*, another mineral from the same locality, forms rhombic crystals in which $a : b : c = 0.94351 : 1 : 0.9299$. Observed forms: P , $\frac{1}{2}P\bar{\infty}$, $2P\bar{\infty}$, $\infty P\bar{\infty}$, $\infty P\bar{\infty}$, and $0P$. The crystals are tabular parallel to $\infty P\bar{\infty}$, and cleave perfectly parallel to $\infty P\bar{\infty}$, imperfectly parallel to $0P$. According to Des Cloizeaux, the plane of the optic axes is parallel to $\infty P\bar{\infty}$, and the first median line is perpendicular to $0P$. Dispersion of axes considerable; $\rho < \nu$.

The mineral dissolves in nitric and in hydrochloric acid at ordinary temperatures. It contains no ammonia. Its analysis gave 41.25 per cent. P_2O_5 , 35.73 H_2O , and (by difference) 23.02 MgO , leading to the formula $2MgO, P_2O_5 + 7aq$.

Mispickel, $FeSAs$, from Pribram. By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1880, **1**, Ref. 41). This mineral is found in the Pribram veins (Adalbertigang) in crystals exhibiting the combination ∞P , $0P$, rarely with $P\bar{\infty}$, accompanied by bournonite, blende, calcspar,

galena, dolomite, and boulangerite; in one vein also by crystals of dopplerite. Sp. gr. 5.9 (according to older statements 6 to 6.2). Analysis gave 21.27 per cent. S, 43.99 As, and 34.74 Fe, the formula requiring 19.63 S, 46.01 As, and 34.36 Fe. Measurements of the angles of the crystals are given in the paper, but they are only approximate, as the faces were too much curved and channelled to admit of exact measurement.

The same paper also contains crystallographic notices of *calcite* and *cerusite* from the Bleiberg, *sulphur* from the Petzen, near Miss, and *pyrites* from the Böckstein, in Salzburg. H. W.

Halotrichite and Melanterite from Idria. By V. V. ZEPHAROVICH (*Wien. Akad. Ber.*, 79, 1879; *Jahrb. f. Min.*, 1880, 1, Ref. 18).—In the "Old Man" mine at Idria, two salts were found in 1878 forming kidney-shaped and botryoidal crusts of various thicknesses up to 4 cm. The more abundant of the two is a pale to dark reddish-yellow salt, exhibiting on the transverse section either fibrous or porous to honeycomb-shaped groups. The analysis of carefully selected material showed that the mineral had essentially the composition of an alum (halotrichite):— $(\frac{2}{3}\text{Fe}\frac{4}{3}\text{Mg})\text{O}$, $(\frac{9}{10}\text{Al}\frac{1}{10}\text{Fe})_2\text{O}_3$, $4\text{SO}_3 + 24\text{aq}$, altered by loss of water; apple-green in the fresh state.

In this alum, especially on the honeycomb-shaped portions and on the surface, there occurs, together with a small quantity of ferruginous magnesium sulphate (epsomite) a definite iron magnesium sulphate in the form of melanterite, having almost exactly the composition $3(\text{FeSO}_4, 7\text{aq})$, $(\text{MgSO}_4, 7\text{aq})$. This compound is monoclinic, with the axial ratio $a : b : c = 1.1803 : 1 : 1.5420$, and the axial angle $\beta = 73^\circ 36' 37''$. Observed forms 0P , $\text{P}\infty$, ∞P , always with $\text{P}\infty$, — $\frac{1}{3}\text{P}\infty$ $\infty\text{P}\infty$, and only on one crystal the new forms — $3\text{P}\infty$ and $\frac{1}{3}\text{P}\infty$.

To determine the influence exerted by the addition of magnesium sulphate on the forms of the iron-compound, mixtures were made in various proportions, two of which yielded measurable crystals. The results obtained with these and with pure ferroso-ferric sulphate are given in the following table, which shows the variations in the axes a on the one hand, and of the axes c , together with the angle β , on the other ($b = 1$), consequent on a diminishing amount of iron and an increasing amount of magnesium:—

I. $\text{FeSO}_4, 7\text{aq}$ with 25.9 FeO.

II. $7(\text{FeSO}_4, 7\text{aq}) + 2(\text{MgSO}_4, 7\text{aq})$ „ 20.7 FeO and 3.3 MgO.

III. $11(\text{FeSO}_4, 7\text{aq}) + 8(\text{MgSO}_4, 7\text{aq})$ „ 15.8 FeO and 6.4 MgO.

	$a : b : c$	β : $\frac{\text{P}\infty}{\infty\text{P}}$ 100 : 001	$\frac{0\text{P}}{\infty\text{P}}$ 001 : 110	$\frac{\infty\text{P}}{110}$ 110 : 110	$\frac{\text{P}\infty}{101}$ 101 : 110	$\frac{\text{P}\infty}{101}$ 101 : 001	$\frac{\text{P}\infty}{101}$ 101 : 001
I.	1.1828 : 1 : 1.5427	104° 15½'	99° 19'	82° 12'	119° 0'	136° 16'	118° 14'
II.	1.1814 : 1 : 1.5428	„ 19½'	„ 22'	„ 17'	„ 17'	„ 16½'	„ 9'
III.	1.1799 : 1 : 1.5434	„ 26'	„ 27''	„ 23'	„ 23'	„ 18½'	„ 1'

The optical examination of melanterite likewise showed that the crystals are monoclinic, and that the results of v. Kobell and Sauber, from which they inferred that the crystals were triclinic, were due to tensions in non-homogeneous crystals. A homogeneous plate cut parallel to the base gave exactly corresponding results, whereas non-homogeneous sections exhibited variations according to the position in which they were viewed.

H. W.

The Clintonite Group. By G. TSCHERMAK and L. SIPÖCZ (*Wien. Akad. Ber.* [2 Abth.], 78, Nov. Heft; *Jahrb. f. Min.*, 1880, Ref. 25).—This name is applied by the authors to a group of minerals nearly related by their chemical and crystallographic characters to the micas, viz., Seybertite, Clintonite, Brandisite, Xanthophyllite, Chloritoid, Sismondin, Masonite, and Sapphirin.

Xanthophyllite.—Monoclinic. The crystals in their general form resemble those of biotite (magnesia-mica), but do not exhibit the same faces or the same twin-structure. Assuming the same primary form as that adopted by Biot for biotite, the observed faces of xanthophyllite will be represented by the symbols $0P$, $+\frac{1}{2}P\infty$, $-\frac{3}{4}P3$, $\frac{2}{3}P\infty$, $+\frac{1}{3}P$. They are isomorphous with those of meroxene, and often very complex in structure, each individual lamina consisting of several, usually three, individuals inclined to one another at 120° , having the basal face $0P$ in common with the laminae grouped in twins like those of mica. The plane of the optic axes is parallel to $\infty P\infty$; their angle varies from 17° to 32° . Negative. Dispersion none, or $\rho < v$. Xanthophyllite gives percussion- and pressure-figures like those of mica, but opposite in position, the percussion-figures of each of these two minerals corresponding in position with the pressure-figures of the other. The same is true with regard to brandisite and seybertite. Corrosion with sulphuric acid produces on the basal face sunk triangular pyramids, whose sides are parallel to the edges $0P/+\frac{1}{2}P\infty$, $0P/-\frac{3}{4}P3$, and $0P/+\frac{1}{3}P$.

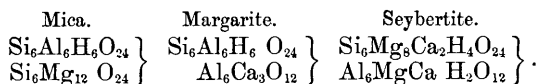
Brandisite.—Monoclinic; crystals always twinned. The individual crystals have the same complex structure as those of xanthophyllite. Observed faces $0P$, $-\frac{1}{2}P$, $+\frac{3}{2}P$, $+\frac{6}{7}P$, $+2P$, $\frac{1}{2}P\infty$, $\frac{5}{2}P\infty$, $9P\infty$, $\infty P\infty$. The faces, with exception of $0P$, are all different from those of xanthophyllite, but the angles between them, which are nearly the same as in meroxene, show a distinct resemblance of these forms to those of mica. The optic axes lie in the plane of symmetry. Axial angle = 18° to 35° . Dispersion not observed.

Seybertite (commonly called Clintonite).—Monoclinic. Isomorphous with brandisite. Longish, thick six-sided tablets from Amity and Warwick exhibited numerous but ill-defined side-faces, on which account only a few of them could be determined: $0P$, $+2P$, $+\frac{3}{2}P$, $+\frac{1}{4}P$, $\frac{5}{2}P\infty$, $\frac{5}{6}P\infty$, $\frac{2}{3}P\infty$. The edge-angles of these crystals (also those of brandisite) are nearly equal to the corresponding angles of meroxene. The plane of optic axes is perpendicular to the plane of symmetry. Double refraction negative. Dispersion imperceptible. Axial angles 3 — 13° .

The chemical analysis of the three minerals above described did not lead to any simple formula, whence it may be inferred that they con-

sist of isomorphous mixtures of at least two distinct compounds. The discussion of their analyses leads to the conclusion that they contain a mixture of an aluminate with a silicate, the two containing about equal quantities of lime. The authors regard them as mixtures of the two members $\text{Si}_6\text{Mg}_5\text{Ca}_2\text{H}_4\text{O}_{24}$ and $\text{Al}_6\text{MgCaH}_2\text{O}_{12}$ (not known in the separate state), which are present in xanthophyllite in the ratio 5 : 8, in brandisite of 3 : 4, and in seybertite of 4 : 5, a sensible amount of fluorine in the last-named mineral being here disregarded. The composition of the minerals calculated on these assumptions agrees satisfactorily with the analytical results.

Margarite, both by its physical properties and by its chemical relations, forms a link between the micas and the minerals of the clintonite group. Its analyses lead to the formula $\text{Si}_6\text{Al}_{12}\text{Ca}_3\text{H}_6\text{O}_{36}$, which may be resolved into a silicate and an aluminate, $\text{Si}_6\text{Al}_6\text{H}_6\text{O}_{24} + \text{Al}_6\text{Ca}_3\text{O}_{12}$. The silicate is identical with the first of the two silicates which Tschermak supposes to exist in the magnesia micas; a corresponding aluminate occurs in seybertite. The latter again is related to mica by the similarity of the silicates $\text{Si}_6\text{Mg}_{12}\text{O}_{24}$ and $\text{Si}_6\text{Mg}_5\text{Ca}_2\text{H}_4\text{O}_{24}$, both being of the olivine type. These relations are more clearly shown by the following comparison:—



The following minerals, according to their physical properties and chemical constitution, are also allied to the clintonite group.

Chlorite-spar.—Monoclinic. Black, elongated, six-sided tablets from Pregratten in Tyrol, built up of a series of thin laminæ, grown together like twin-crystals, and inclined to one another at 120° . The crystals are never simple; they exhibit optically different striæ, as in xanthophyllite. Observed faces $0P$, $-\frac{3}{2}P$, $+P$, $P\infty$, $6P\infty$. Cleavage parallel to $0P$ not nearly so distinct as in mica, apparently perfect only on account of the twin-formation parallel to $0P$. Plane of optic axis parallel to $\infty P\infty$. First median line inclined at about 12° to the normal on $0P$. Positive. Distinctly dichroic. Hardness somewhat above 6·5, as in Sismondin, Masonite, and Ottrelite. Sp. gr. 3·4—3·6. Composition $\text{Si}_2\text{Fe}_2\text{H}_2\text{O}_7 + \text{Al}_4\text{H}_2\text{O}_7$, indicating a slight similarity to the clintonite group.

Ottrelite and *Masonite* agree with chlorite-spar in their optical and chemical characters; the difference between their chemical composition and that of the latter is due to foreign enclosures, without which these two minerals are not obtainable.

Sismondin in its optical characters is also exactly like chlorite-spar, with which it is also isomorphous; but sufficient material for exact determination of its form has not yet been obtained. It appears to be a variety of chlorite-spar containing comparatively less iron, and, therefore, more magnesium than the typical variety. An analysis of sismondin from St. Marcel led to the empirical formula—



Sapphirin.—Monoclinic Form probably somewhat similar to that

of the preceding group. Plane of optic axes nearly parallel to 0P. Negative. Sp. gr. = 3·42—3·47. Composition $\text{Si}_2\text{Mg}_2\text{O}_6 + \text{Al}_6\text{Mg}_2\text{O}_{11}$.

Classification.

Margarite Series.—Margarite (Tschermak and Sipöcz). Syn. Perglimmer (Mohs). Corundellite, Clingmannite (Silliman). Eme-rylite (Smith), Diphanite (Nordenskiöld).

Clintonite Series.—Xanthophyllite (G. Rose). Syn. Walue-wite (v. Kokscharow). Brandisite (Liebener).

Seybertite (Clemson). Syn. Clintonite (Mather). Chrysophane (Breithaupt). Holmite (or Holmesite) (Thomson).

Chloritoïd Series.—Chlorite-spar (Fiedeler). Syn. Chloritoïd (G. Rose). Barytophyllite (Glocker). Masonite (Jackson). Phyl-lite (Thomson). Ottrelite (Des Cloizeaux and Damour). Sismondin (Delesse).

Sapphirin (Giesecke).

H. W.

Green Garnet from Val Malenco. By A. COSSA (*Gazzetta*, 10, 469—470).—In a specimen of asbestos from Val Malenco, in the Valtel-line, a mineral was discovered consisting of spherical nodules built up of minute crystals of a bright green colour, and which at first sight appeared to be olivine. The crystals are perfectly transparent, and on some of their surfaces rhombododecahedral faces could be observed. Fracture conchoidal, and hardness about the same as that of quartz. It does not melt very easily, and gives a green glass. When heated in an open crucible, it acquires a rusty colour, and the weight is slightly increased. The analytical results correspond with the formula $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$. Garnets of nearly the same composition found in asbestos at Zermatt were analysed by Damour in 1879. C. E. G.

Thaumasite, a New Mineral from Aareskutan. By G. LINDSTRÖM (*Jahrb. f. Min.*, 1880, Ref., 37).—The material for analysis was collected at different times in the Bjelkegrube, near Aareskutan (Jemtland, Sweden); one specimen consisted of a perfectly homo-geneous aggregate of apparently rhombic fibres. The mean of three closely agreeing analyses gave—

SiO_2 .	CO_2 .	SO_3 .	CaO .	Al_2O_3 .	Na_2O .	K_2O .	Cl.	H_2O .
9·70	6·86	13·02	27·28	0·16	0·11	0·08	0·12	42·20 = 99·53,

agreeing very nearly with the formula CaSiO_3 , CaCO_3 , CaSO_4 + $14\text{H}_2\text{O}$.

Thaumasite is white, with a faint fatty lustre; translucent, and has a flat conchoidal fracture. Hardness = 3·5. Sp. gr. = 1·877 at 19°. Before the blowpipe it does not fuse, but swells up, becomes rugged, and colours the outer flame red. With phosphorus salt it forms a colourless bead, with a skeleton of silica. At 100° the water is given off slowly, and not quite completely. According to Engberg, thauma-site occurs filling clefts and cavities, and is soft and kneadable while in the mine, but hardens quickly on exposure to the air.

Thaumasite is often accompanied by a finely fibrous, chalk-white

mineral having a hardness of 1·5 to 2·5, and containing 11·85 per cent. SiO_2 , 13·61 SO_3 , 25·74 CaO , 2·58 Al_2O_3 , and 6·86 CO_2 . This mineral is probably a decomposed thaumasite, a perfectly similar product being often found as a coating on the latter. H. W.

Eggonite. By A. SCHRAUF (*Zeitschr. f. Krystallographie*, **3**, 352—356).—A cadmiferous zinc silicate, found in small crystals on druses of chrysocolla crystals occurring in a small lump of large-grained light brown calamine from Altenberg. These small crystals, differing in form and colour from those of the chrysocolla, were recognised as belonging to a new mineral species, to which the name of *eggonite* was given. The crystals of this mineral, from $\frac{1}{2}$ to 1 mm. in size, are of a light brown colour, and transparent to translucent. Streak white. Lustre imperfectly adamantine. The crystals are triclinic, with the axial ratio $a : b : c = 1.3260 : 1 : 0.7989$; and the axial angles $\alpha = 90^\circ 23'$, $\beta = 90^\circ 50'$; $\gamma = 91^\circ$. A twin-formation according to $\infty P\infty$ occurring in some of the crystals, converts the asymmetry into an apparent monosymmetry; observed faces $\infty P\infty$, $\frac{2}{3}P\infty$, $\frac{2}{3}P'\infty$, $\infty P\frac{3}{2}$, $\infty P'\frac{3}{2}$, $\infty P\infty$. Morphologically eggonite is nearly related to the rare mineral *hopeite*, and to *chrysocolla*, but it does not exhibit the hemimorphism of the latter, and its refractive indices differ from those of the former. Eggonite is infusible; gives on charcoal a deposit of cadmium without zinc; is insoluble in acids; gives a siliceous skeleton on a bead of phosphorus salt. H. W.

Mineralogical Notices. By A. v. LASSAULX (*Zeitschr. f. Krystallographie u. Mineralogie*, 1879, **3**, 3; *Jahrb. f. Min.*, 1880, **1**, Ref. 43).—(1). A mineral from the rock of Monte Calvario, near Biancavilla, on Etna, designated by Blum, Des Cloizeaux, and others, as *brookite*, has been found by v. Lassaulex to be identical with the mineral from the Arany Berg, in Transylvania, designated by A. Koch (*Zeitschr. f. Kryst.*, **3**, 307) as *szaboite*. It forms very thin, brown-red plates, from 0·5 to 2 mm. long, and belonging to the triclinic system, although they form combinations resembling those of augite. Observed forms, $\infty'P$, $\infty P'$, $\infty P\infty$, P , P' , $0P$, $2P\infty$, $2'P\infty$. The author considers that the crystals on which Koch found all the four quarter-pyramids were twins combined according to the ordinary augite law. The crystals exhibit cleavage-directions not quite coinciding with the position of the combination-edge $\infty P : P$. Parallel to this and to the vertical axis are imbedded numerous lamellæ of ferric oxide, so that some of the individuals appear quite brown and opaque. Lighter-coloured crystals exhibit a distinct dichroism, appearing light greenish-yellow when the vertical axis is placed parallel to the principal section of the lower Nicol; brown-yellow when it is perpendicular thereto. The plane of the optic axes appears to have a position different from that in augite.

The crystals when examined with the blowpipe, give the iron reaction with borax, and a slight siliceous skeleton with phosphorus salt.

If the amount of iron found by Koch be calculated as monoxide, a formula will be obtained very near to those of rhodonite and augite. Crystallographically, also, the mineral is very nearly related to the

triclinic augites, as will be seen from the following angular measurements :—

$\infty P\infty : \infty'P$	$= 136^{\circ} 10'$	134°
$\infty P\infty : \infty P'$	$= 131 28$	$133 30'$
$\infty P\infty : \infty P'$	$= 134 01$	$134 59$
$\infty P\infty : \infty'P$	$= 138 21$	$137 37$

Szaboite may therefore be regarded as a triclinic member of the pyroxene group, very nearly related to augite.

(2.) *Szaboite* from Riveau Grand, on the Mont Dore.—Minute crystals from this locality appear from their general appearance, as well as from microscopic measurements and blowpipe reactions, to consist of szaboite. Their complete opacity, however, rendered a determination of their crystalline form impossible.

(3.) *Iron-glance* from Biancavilla exhibits many-faced combinations of various habit. Observed forms: R, $-R$, $-\frac{1}{2}R$, $-2R$, $-\frac{1}{6}R$, $\frac{4}{3}P2$, $\frac{2}{3}P2$, $\infty P2$, $\frac{1}{5}R3$, $\frac{2}{5}R3$, $0R$. The face $-R$ occurs but very rarely, having been observed only on a single crystal, as a perpendicular truncation of the edges of $\frac{4}{3}P2$. The types which occur most frequently are:—1. Tabular type: very thin tablets according to $0R$, with R, $\infty P2$, and rarely $-\frac{1}{2}R$.—2. Rhombohedral type: R predominant, with $\infty P2$, $-\frac{1}{2}R$, $0R$, and rarely $\frac{1}{5}R3$.—3. Pyramidal type: $\frac{4}{3}P2$ predominant, with $\frac{2}{3}P2$, $\infty P2$, $\frac{1}{2}R$, $-\frac{1}{2}R$, and rarely $-\frac{1}{6}R$ and $-2R$. Twins occur according to the laws, twin-axis perpendicular to ∞R , and twin-axis perpendicular to R. The twins according to the first law are mostly elongated in the direction of the twin-axis, and rarely exhibit the twin-boundary on $0R$; in some cases they exhibit a sharply defined feathery striation. Twins according to the second law generally consist of a large crystal, on which, in various mutually crossing directions, smaller crystals are implanted in twin fashion; or else there are only two crystals of the pyramidal type, which are then united in swallow-tail forms. These latter further unite into four-fold groups, new twins with their twin-axes in exactly similar directions being continually added, and partially also producing intersection twins.

H. W.

Fall of Meteorites at Gnadenfrei, in Silesia. (*Jahrb. f. Min.*, 1880, 1, Ref. 46).—This fall took place on the 17th of May, 1879. The largest of the stones found weighed 0.75 kilo.; its fall was observed by several persons, and was accompanied by a loud detonation. The stone sank into the ground a foot deep; it was covered with a black crust, and was cold when taken up immediately after falling. 3 kilos. from this was found another stone, which broke into several pieces when taken up. According to v. Lasaulx, these meteoric stones belong to the class of chondrites, and are made up of numerous green and white spheres, bound together by a loose cement. The spheres consist partly of olivine, partly of enstatite. Sparingly imbedded in the mass are metallic particles, consisting of nickel-iron, magnetic pyrites, and troilite.

H. W.

Products from a Crater. By DAUBREÉ (*Compt. rend.* 91, 949—950).—The paper relates to the crater of a volcano in the Island of

Dominica, one of the Antilles. The lake of boiling water which filled the crater at the time of the eruption of January, 1880, had disappeared by the April following, and the crater was dry, except at one point, whence issued a stream of blackish boiling water. The analysis of a sample of this water, taken from the centre of the boiling spring, showed that 1 litre held in solution—

KCl.	NaCl.	CaS.
0·370	0·500	0·045 gram.

Other samples collected at various points of the streams issuing from the hot spring, showed, however, very different quantities of salts. 38 c.c. of the water taken from the spring itself held in suspension 24 grams of solid matter, 92·2 per cent. of which consisted of silica and alumina; 5 per cent. of oxide of iron; 1·6 per cent. of calcium carbonate; 0·2 per cent. of magnesium carbonate; 0·5 per cent. of sulphur in the state of pyrites. These waters were remarkable for the large quantity of potassium chloride contained in them, amounting in one sample to 4·21 grams per litre.

R. R.

Action of Mineral Waters on Metals. By DAUBRÉE (*Compt. rend.*, 92, 57—59).—The paper relates to the remains of antique medals recently discovered at a thermal spring at Baracci, in the commune of Olmeto, Corsica. Some of the coins were simply blackened on the surface by a superficial oxidation; in others, all but a thin disc of the metal was eaten away and converted into a thick layer of confused crystals, having a blackish colour and a metallic lustre. Apparently these consist of a double sulphide of tin and copper, the metals contained in the bronze.

R. R.

Organic Chemistry.

Chlorine and Bromine Derivatives of Methane. By A. DAMOISEAU (*Compt. rend.*, **92**, 42—44).—When a current of chlorine, mixed with methyl chloride, is made to pass through a tube containing animal charcoal, heated at 250—350°, substitution-products are obtained varying with the proportions of chlorine and chloride employed. It is merely necessary to remove the hydrochloric acid from the vapours by water, and condense them. In this way several hundred grams of chloroform can be rapidly prepared; and if sufficiently pure methyl chloride could be had at a suitable price, chloroform might be advantageously manufactured by this process. The author points out the marked effects produced by animal charcoal in presence of chlorine and bromine at temperatures much below those at which the substances acted on would otherwise be stable. Bromine and methyl bromide will yield at will, according to the proportions in which they are mixed, CH_2Br_2 , CHBr_3 , and CBr_4 , whilst acetic acid when heated in this way with chlorine or bromine yields, not the haloid derivatives of the acid, but, chloroform and bromoform.

R. R.

Action of Antimony Pentachloride on Carbon Bisulphide.

By A. BERTRAND and E. FINOT (*Bull. Soc. Chim.* [2], **34**, 201).—The antimony trichloride and sulphur which, according to Vilein, are formed, together with carbon tetrachloride, when antimony pentachloride reacts on carbon bisulphide, are due to the decomposition of antimony sulphochloride, which is first formed. This is seen by conducting the reaction at a low temperature, when crystals of the sulphochloride separate out; on heating slowly these decompose into antimony trichloride and sulphur. The reactions are, $2\text{SbCl}_5 + \text{CS}_2 = 2\text{SbCl}_3\text{S} + \text{CCl}_4$; and $\text{SbCl}_3\text{S} = \text{SbCl}_3 + \text{S}$. L. T. O'S.

Preparation of Ethyl-vinyl Hydrocyanide. By O. DE CONINCK (*Bull. Soc. Chim.* [2], **34**, 633).—In an attempt to prepare this compound, 280 grams of isobutyl iodide were heated with 700 grams of the double salt $\text{HgCy}_2\cdot\text{KCl}$, but the products of the reaction were mercuric iodide, hydrocyanic acid, and butylene, with a trace of an organic cyanide. Under the conditions of the experiment, the secondary hydrocyanide, $\text{Me}\cdot\text{CH}_2\cdot\text{CHCy}\cdot\text{Me}$, first formed, splits up into hydrocyanic acid and dimethyl-ethylene, $\text{MeCH}:\text{CHMe}$. Since the original isobutyl iodide was a derivative of ethyl-ethylene, this latter has been converted into the isomeric dimethyl-ethylene. C. H. B.

Products from Petroleum Coke. By L. PRUNIER and E. VARENNE (*Bull. Soc. Chim.*, **33**, 567—572, and *Compt. rend.*, **90**, 1006).—The residue left in the retorts in the rectification of petroleum, and called by the authors "le coke de pétrole," is a dark, spongy, brittle mass easily powdered, a portion of which is soluble in carbon bisulphide. This soluble portion may be separated by means of alcohol, ether, and glacial acetic acid into various fractions; the one soluble in alcohol is an oxygenated pale yellow viscous substance; the ethereal solution yields a mixture of orange-coloured crystallisable hydrocarbons and oxygenated compounds, whilst the portion soluble in acetic acid is dark brown, and seems to be the substance to which the fluorescence of petroleum is chiefly due. If the carbon bisulphide extract is submitted to fractional distillation in a vacuum, about one-fourth passes over below 450° ; this is a mixture of various substances, all of which are strongly fluorescent, and some crystalline. These products are being investigated. C. E. G.

Potassium Propargylate. By E. BANDROWSKI (*Ber.*, **13**, 2340—2342).—An aqueous solution of acid potassium acetylenedicarboxylate is decomposed by a gentle heat, with formation of carbonic anhydride and potassium propargylate: $\text{C}_4\text{KHO}_4 = \text{CO}_2 + \text{C}_3\text{KHO}_2$. The compound $\text{C}_3\text{KHO}_2 + \text{H}_2\text{O}$ forms transparent prismatic crystals, which explode at 105° . The silver and cuprous propargylates are also explosive. W. C. W.

Preparation of Potassium Ferricyanide. By K. SEUBERLICH (*Dingl. polyt. J.*, **338**, 482—484).—The author has undertaken this work with a view of ascertaining the correctness of a statement, published in several journals some time ago, that potassium ferricyanide is obtained by boiling a strongly alkaline solution of potassium fer-

rocyanide with peroxide of lead. It was found that after boiling this mixture for several hours with an excess of the oxide, taking care to exclude it from the action of atmospheric carbonic acid, not a trace was converted into ferricyanide. A better result was obtained by boiling a perfectly neutral solution of potassium ferrocyanide with an excess of peroxide of lead in a flask fitted with a vertical condenser tube, 21.8 per cent. of the potassium ferrocyanide being then converted into ferricyanide. By grinding an aqueous solution of pure potassium ferrocyanide with an excess of peroxide of lead in a mortar, and digesting the mixture for two hours at the ordinary temperature, 12.95 per cent. was transformed into potassium ferricyanide.

It was supposed that the further conversion of potassium ferrocyanide into ferricyanide was prevented by the potash which is liberated in the reaction: hence the effect of neutralising the latter with a strong acid was tried. 10 grams of potassium ferrocyanide dissolved in 50 c.c. of water were treated with an excess of peroxide of lead and the requisite quantity of dilute hydrochloric acid, agitating the mixture the whole time. In this way it was possible to convert the whole of the potassium ferrocyanide in the cold into the corresponding ferricyanide; it may, however, be found desirable to add a slight excess of hydrochloric acid to ensure complete conversion. If after filtration the excess of the acid is neutralised with soda, a pure salt is obtained on evaporation, the mother-liquor containing no other impurities than the chlorides of potassium and sodium. D. B.

Magnesium-Potassium Platinocyanide. By A. RICHARD and A. BERTRAND (*Bull. Soc. Chim.* [2], 34, 630).—The double platinocyanide of magnesium and potassium, $K_2PtCy_4.MgPtCy_4.7H_2O$, was obtained in the manner described by Wurtz (*Diét.*, i, 1117). It crystallises in colourless hexagonal prisms, terminated by faces of the rhombohedron. Angle of rhombohedron = $101^\circ 5'$; of rhombohedron on prism = $136^\circ 50'$; ratio of horizontal to vertical axis = 1.07; cleavage parallel to the prismatic faces. The prisms were much elongated, and the three faces perpendicular to the planes of symmetry of the rhombohedron were much more developed than the other three. A plate cut perpendicular to the principal axis gave, with polarised light, coloured circular rings with a black cross.

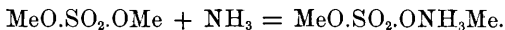
The platinocyanic acid was estimated in the form of silver platinocyanide, which is insoluble in nitric acid. C. H. B.

Combination of Titanium Tetrachloride with Ethyl Ether. By A. BERTRAND (*Bull. Soc. Chim.*, 33, 566).—When the vapours of ether and titanium chloride are mixed, they unite, forming a crystalline compound of a yellowish-green colour. It resembles the compounds obtained under similar circumstances with the chlorides and bromides of tin, antimony, and bismuth. C. E. G.

Action of Ammonia and Amines on Ethyl and Methyl Sulphates. By P. CLAEISSON and C. F. LUNDVALL (*Ber.*, 13, 1699—1705).—This subject has already been studied by Dumas and Peligot (*Ann. Chim. Phys.*, 58, 32) and by Strecker (*Annalen*, 75, 45). The action of ammonia and of amines on methyl or ethyl sulphates is usually very

energetic, and in some cases attended with explosions; to control the action the sulphates are dissolved in ether or benzene. Ammonia or substituted ammonias, when in excess, react on the methyl or ethyl sulphates, producing the hydrogen-methyl or hydrogen-ethyl sulphates together with an ammonia base containing one alcohol radical more than the original base. If, however, the sulphates are in excess, hydrogen-methyl or hydrogen-ethyl sulphate is obtained together with a higher substituted base, more generally an ammonium base. Benzene forms liquid molecular compounds with some of these salts. The mode of investigating the products of the various reactions adopted by the authors usually consists in distilling them with potash and converting the free base into its hydrochloride, and then into the platinochloride. In the case of the more volatile ammonium bases, their salts with ethyl- or methyl-sulphuric acid were decomposed by potash, and the potassium-ethyl sulphate removed by crystallising from an alkaline solution.

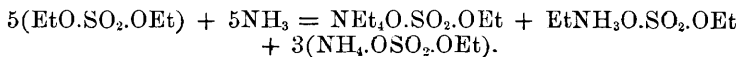
Ammonia reacts on methylsulphate, and, producing methylamine methylsulphate, which crystallises in needles or scales, is easily soluble in water and deliquesces on exposure. Its formation is expressed as follows:—



A small quantity of ammonium methylsulphate is also produced; if methylsulphate is in excess, the reaction is more complicated, and the products are similar to those obtained with ethylsulphate.

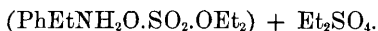
Ethylamine reacts energetically with an excess of dimethylsulphate, but the platinochlorides of the bases could not be separated: diethylamine gives diethylamine and diethyldimethylammonium methylsulphate, whereas with triethylamine there is only triethylmethylammonium methylsulphate formed. Aniline and methylsulphate give methyl-aniline methylsulphate, which crystallises in long slender greenish-yellow needles. With dimethylaniline, trimethylphenylammonium methylsulphate has been obtained; it crystallises in long stellate-grouped needles. With paratoluidine, liquid methylparatoluidine methylsulphate is obtained. The platinochloride of methylparatoluidine crystallises in beautiful red rhombic crystals. Orthotoluidine yields no crystalline product. Tribenzylamine dissolved in benzene and heated with methylsulphate at 100° in sealed tubes, yields methyltribenzylammonium methylsulphate, crystallising in stellate-grouped prisms or leafy scales. The platinochloride of the base is a pale yellow very insoluble precipitate.

Ammonia reacts with ethylsulphate producing the ethylsulphates of ammonium, ethylammonium, and tetrethylammonium, thus:—



Ethyl sulphate and ethylamine yields a result similar to that obtained with methyl sulphate; with diethylamine, triethylammonium ethylsulphate was obtained; it is a liquid; with triethylamine, tetrethylammonium ethylsulphate was obtained. The solutions of ethylsulphate and aniline in benzene act on one another at ordinary temperatures, yield-

ing a crystalline product, a compound of ethyl sulphate and ethylphenylammonium ethylsulphate, having the composition



It crystallises in long shining prisms. Simultaneously an oil is formed, which is a molecular compound of benzene and ethylaniline ethylsulphate, and when heated at 140° it is decomposed, leaving a crystalline mass of ethylaniline ethylsulphate. The products obtained from ethylsulphate and dimethylaniline, paratoluidine, and orthotoluidine are analogous to those obtained from methylsulphate and these compounds.

From the above results, the authors conclude that the neutral sulphates of alcohol-radicals act with ammonia and substituted ammonias in the same manner as the nitrates and chlorides. P. P. B.

Reduction of Ethyl Nitrate by Alcohol. By A. BERTRAND (*Bull. Soc. Chim.*, **33**, 366—367).—When an alcoholic solution of silver nitrate is boiled for some time with ethyl iodide or bromide, silver iodide or bromide is formed, but the liquid on being distilled does not yield ethyl nitrate. An examination of the product showed that it contained, besides unaltered alcohol, acetaldehyde and ethyl nitrite, and apparently ethyl acetate in small quantity. The author considers that the nascent ethyl nitrate is reduced by the alcohol at the instant of its formation in the following way: $\text{EtNO}_3 + \text{C}_2\text{H}_5.\text{OH} = \text{EtNO}_2 + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. He intends to ascertain whether it is indispensable that the ethyl nitrate should be in the nascent state for this reaction to occur, and whether the reaction is a general one.

C. E. G.

Di-iodopropyl Alcohol and Moniodallyl Alcohol. By H. HÜBNER and LELLMAN (*Ber.*, **14**, 207—209).—*Di-iodopropyl alcohol*, $\text{C}_3\text{H}_5\text{I}_2\text{OH}$, is obtained as a crystalline mass (m. p. 45°), when 25 grams of iodine are dissolved in 10 grams of allyl iodide. The compound is soluble in alcohol, ether, chloroform, and benzene. When a solution of di-iodopropyl alcohol in chloroform is heated to its boiling point and allowed to cool, moniodallyl alcohol is deposited in colourless prisms (m. p. 160°), which are soluble in alcohol, chloroform, and acetic acid. This compound is not acted on by benzoic chloride or by acetic anhydride.

W. C. W.

Supposed Synthesis of Glucose. By L. VALENTE (*Gazzetta*, **10**, 540—543).—This is a criticism on a paper by S. Zinno, in which he professes to have obtained glucose by treating an aqueous solution of glycerol with potassium permanganate, precipitating the potash with tartaric acid, removing the excess of tartaric acid with powdered marble, and evaporating. He states that the residue has all the properties of glucose, and that the solution is dextrorotary. The author has repeated his experiments and finds that there is no glucose present, the action on polarised light being due to the calcium tartrate which remains dissolved. Kossmann (*Bull. Soc. Chim.*, **28**, 246) in 1877 made a similar assertion as to the transformation of glycerol into glucose, which was completely refuted by Liebermann (*Ber.*, **10**, 2095).

C. E. G.

Strobometric Observations on the Inversion of Cane-sugar by Concentrated Hydrochloric Acid at the Ordinary Temperature. By F. URECH (*Ber.*, 13, 1696—1697).—These observations show that the inversion of cane-sugar by hydrochloric acid takes place at 23°; it, however, requires some time for its completion, viz., from 6—7 hours. The change takes place rapidly at first, and gradually becomes slower as the completion of the inversion approaches.

P. P. B.

Specific Rotation of Cane-sugar in different Solvents. By B. TOLLENS (*Ber.*, 13, 2297—2303).—The author observes that a solution of sugar in methyl and ethyl alcohols and in acetone exhibits higher specific rotation than the aqueous solution. The following numbers were obtained with a 10 per cent. solution of sugar:—

Solvent.	Specific rotation α_D .
Water	66·667°
Ethyl alcohol and water.....	66·827
Methyl alcohol and water	68·628
Acetone and water	67·396

W. C. W.

Oxidation of Lactose and Lactonic Acid by Silver Oxide. Preparation of Lactonic Acid. By H. KILIANI (*Ber.*, 13, 2307—2308).—An aqueous solution of lactose is oxidised by the action of silver oxide at 50°, with formation of oxalic, glycollic, and lactonic acids. Lactonic acid is easily prepared by leaving a solution of milk-sugar (1 part) in contact with 2 parts of bromine for 24 hours. After removing the excess of bromine by warming the liquid on the water-bath, the cold solution is treated with silver oxide. The silver is precipitated by sulphuretted hydrogen and the filtrate boiled with cadmium carbonate. On cooling, the liquid deposits crystals of cadmium lactonate.

W. C. W.

Identity of Arabinose and Lactose. By H. KILIANI (*Ber.*, 13, 2304—2306).—The crystalline sugar which Scheibler (*Ber.*, 1, 58 and 108; 6, 612; this Journal, 1873, 1124) obtained by the action of dilute sulphuric acid on gum arabic, and to which the name of *arabinose* was given, is shown to be identical with lactose by its specific rotation and by the changes it undergoes when treated with sodium amalgam or nitric acid.

W. C. W.

Inulin. By H. KILIANI (*Annalen*, 205, 145—190).—The author at the outset alludes to the discordant results of former researches on inulin and to the necessity of a fresh study of its properties and chemical relations. In order to prepare it, roots of the *Dahlia variabilis* and *Inula helenium* were boiled with water in the presence of sodium carbonate. The liquid obtained was cooled by a freezing mixture, and the separated precipitate was dissolved in hot water, filtered, and again exposed to a freezing mixture. After repeating this process three or four times, the inulin is obtained perfectly white and is subsequently purified from levulose by absolute alcohol, and finally dried over sulphuric acid.

Inulin obtained in this way is a white powder resembling starch; by slow evaporation of an aqueous solution it forms "crystal spheres," as observed by Sachs and Prantl (*Jahresb.*, 1870, 849). It is insoluble in absolute alcohol, sparingly soluble in dilute alcohol and cold water, but very soluble in hot water. The author has confirmed the formation of a gum-like and horny modification of inulin; the latter the author considers to be a highly hydrated inulin, which is converted into solid lumps of inulin in the same way that ferric hydrate and silicic acid are converted into their corresponding anhydrous oxides. Its sp. gr is 1.3491, and its optical rotatory power, as determined with a Wild's polaristobrometer, $[\alpha]_D = 34.6$ to 36.4 , gives results agreeing with those of Lesceur and Morelle (this Journal, 1878, 970). The author assigns to inulin the composition $C_{36}H_{62}O_{41} (= 6C_6H_{10}O_5 + H_2O)$; he has also confirmed the observations of others that inulin, when heated with water in sealed tubes at 100° , is converted into a sugar which resembles levulose in chemical and physical properties. When oxidised with dilute nitric acid, inulin yields formic, oxalic, racemic, glycollic, and probably glyoxylic acids. The author finds that glycollic and saccharic acids alone are formed when dextrin is oxidised with dilute nitric acid.

Inulin is slowly oxidised by long contact with bromine in sealed tubes, with formation of bromoform and carbonic and oxalic acids; the hydrobromic acid formed in the reaction converts the unchanged inulin into levulin. This latter, by the further action of bromine, gives the same products as inulin. By heating the brominated liquid with silver oxide, some of the unchanged levulose is converted into glycollic acid. As this acid is formed by the direct action of bromine and silver oxide, it is possible that the inulin is converted by the bromine into levulose, which is then oxidised by the silver oxide into glycollic acid; for comparison the author has studied the action of bromine and silver oxide on dextrose, and finds that no oxalic, but only gluconic acid is formed, according to the equation $C_6H_{12}O_6 + O = C_6H_{12}O_7$. Glycollic acid is formed as a secondary product of the action of silver oxide on the gluconic acid. By distillation of inulin with hydriodic acid, a small quantity of an oil containing iodine is obtained, but its constitution could not be ascertained, as it readily decomposed. By the action of nascent hydrogen on inulin (sodium amalgam and water) neither mannitol nor mannitan is formed. Pure inulin reduces ammoniacal silver solution and gold chloride, but not Fehling's solution nor gold nor platonic chloride.

When inulin is heated with baryta-water it is partly converted into fermentation lactic acid. By inversion, inulin is not converted at ordinary temperatures nor at $40^\circ C$. into levulose (Barth, *Ber.*, 11, 474; 1878, 591). It appears from these properties that inulin stands in near chemical relation to levulose, and is probably its anhydride. This is shown by the readiness with which it takes up water in many reactions, being converted into levulose. It, however, differs from levulose by not reducing Fehling's solution, and not undergoing fermentation with yeast, and not forming an additive compound with hydrogen. Levulose, the hydrate of inulin, differs from dextrose in its oxidation products with nitric acid and bromine-water; the former gives glycollic and

oxalic, the latter gluconic acid. This difference may be simply explained by supposing dextrose to be the aldehyde whilst levulose is the ketone of mannitol.

V. H. V.

Relation between Crystalline Form and Rotatory Power of certain Carbohydrates. By C. SCHEIBLER (*Ber.*, 13, 2319—2320).—In the following series of carbohydrates—trehalose, $C_{12}H_{26}O_{13}$; arabinose, $C_{12}H_{24}O_{12}$, and saccharine, $C_{12}H_{20}O_{10}$,—the optical rotatory power diminishes and the relation of the vertical axis c to the axes a and b increases as the amount of water in the carbohydrates decreases.

W. C. W.

Optical Rotatory Power of the Carbohydrates and their Derivatives. By T. THOMSEN (*Ber.*, 13, 2264—2266, 2266—2269; 14, 134—140, and 158—162).—The author finds that a simple relation exists between the composition and the rotatory power of the carbohydrates, viz., the rotatory power multiplied by the molecular weight of the substance gives a multiple of the constant, 19. The more dilute the solution, the more closely does it follow this law. For solutions of the ideal concentration $c = 0$ we have the following numbers:—

	$[\alpha]_D \times \frac{\text{mol. wt.}}{100}$
Cane-sugar	$66.75 \times 3.42 = 228.280 = 12 \times 19.024$
Dextrose	$47.625 \times 1.98 = 94.892 = 5 \times 18.978$
Lactose	$52.69 \times 3.42 = 189.684 = 10 \times 18.968$

The molecular rotation $\frac{m[\alpha]_D}{100}$ of the carbohydrates and their compounds is a simple multiple of the common constant 19.0, and the law is exact when the concentration $c = \frac{1}{\infty}$.

An examination of the rotatory power of 51 carbohydrate derivatives confirms the accuracy of this law. The following table shows that the factors vary with the different derivatives of the same carbohydrate:—

	Factors for			
	Carbohydrate.	Acetate.	Sulphate.	Glucoside.
Dextrose	5, 10	—	10, 20	10
Diglucose	—	20	—	—
Milk-sugar	6, 10, 16	10, 12	32	—
Lactoglucose	6	—	—	—
Galactose	9	—	18	—
Cane-sugar	12	14	10	—
Amylum	14, 16	16	20	—
Dextrin	14, 15, 16	—	20	—
Cellulose	—	—	16	—
Wood-gum	5, 7	—	—	—
Inulin from dahlia ..	4, 6	3, 4	—	—
„ chicory	6	—	—	—
„ elecampane	5, 6	6, 7	—	—

The following substances have only one factor :—

Sorbin, 4	Melezitose, 15	Mycose, 30
Phlorose, 4	Arabic acid, 16	Trehalose, 36
Saccharin, 8	Melitose, 16	
Arabinose, 10	Maltose, 24	

In discussing the results contained in this table, the author points out that the probability of the existence of more than one form of dextrin is supported by the variation exhibited in the rotatory power of different aqueous solutions of dextrin.

	$[\alpha]_D$	$\frac{[\alpha]_D \times m}{100}$
Dextrin α	+ 186	302 = 16 \times 18.9
Dextrin β	+ 176	285 = 15 \times 19
Dextrin γ	+ 164.2	266 = 14 \times 19

Specimens of inulin prepared from different sources also exhibit a difference in their rotatory powers.

The molecular rotation of trehalose and mycose are 36 \times 19 and 30 \times 19 respectively.

W. C. W.

Separation of Trimethylamine from the Commercial Hydrochloride. By J. L. EISENBERG (*Ber.*, 13, 1667—1669).—The method proposed depends on the sparing solubility of the platinochloride of trimethylamine in absolute alcohol. The commercial hydrochloride is evaporated to dryness, and the ammonium chloride removed by treatment with absolute alcohol. The alcoholic solution is evaporated to dryness, and then treated with potash, the vapours passing over at 20—30° being absorbed by hydrochloric acid. The solution thus obtained is evaporated to dryness, then taken up with absolute alcohol, and the platinochloride of trimethylamine precipitated by adding platinum chloride. After boiling the precipitate two or three times with alcohol, the platinochloride is obtained in a state of purity. The trimethylamine hydrochloride may be obtained from the platinochloride by removing the platinum with sulphuretted hydrogen, and concentrating the filtrate from the platinum sulphide; 100 c.c. of boiling absolute alcohol dissolves about 2.64 grams of the platinochloride.

P. P. B.

Action of Oxaethylin. By H. SCHULZ (*Ber.*, 13, 2353—2354).—A dose of oxaethylin produces the same effects on animals as atropine does, viz., paralysis of the heart in frogs, and dilatation of the pupil, dryness of the throat, and general excitement in warm-blooded animals.

Chloroxaethylin neither produces dilatation of the pupil nor general excitement. It resembles chloral hydrate in its action on the brain. This may be due to the decomposition of the chloroxaethylin in the system, where the chlorine would neutralise the action of the oxaethylin.

W. C. W.

An Oxygenated Basic Derivative of Aldol. By A. WURTZ (*Compt. rend.*, 91, 1030—1032).—On treating *dialdane* with ammonia

at 100° for two days (*ibid.*, **83**, 1260) a basic product is obtained, which, after separation and purification, is obtained as a colourless, transparent, amorphous mass. The reaction may be thus represented: $-2C_3H_{14}O_3 + 2NH_3 = C_{16}H_{28}N_2O_3 + 3H_2O$. The new base is very soluble in water, alcohol, and ether, and has a marked alkaline reaction. Its solutions by their bitterness resemble those of the natural oxygenated bases. It forms a hydrochloride, having apparently the composition $C_{16}H_{28}N_2O_3 \cdot 2HCl$. R. R.

Aldehyde Resin. By G. L. CIAMICIAN (*Wien. Akad. Ber.* [2 Abth.], 346—357).—The author gives a description of the products which are formed by the action of various reagents on aldehyde resin. The resin was obtained by heating aldehyde with sodium acetate in sealed flasks at 100°, and afterwards distilling off the volatile products.

1. *Reduction with Zinc-dust.*—The oil produced by the reduction is distilled with steam, then by itself, and finally treated with metallic sodium. It is then separated by fractionating into three portions, boiling respectively between 134—136°, 158—160°, and 230—232°. That boiling between 134—136° consists of ethylbenzene, C_8H_{10} : it yields benzoic acid on oxidation. The second portion, boiling at 158—160°, is a mixture of meta- and para-ethyltoluene, C_9H_{12} : on oxidation it yields two acids, the one, soluble in water, and present in largest quantity, is isophthalic acid; the other is terephthalic acid. The third portion of the oil, boiling at 230—232°, consists of methylnaphthalene. It forms a crystalline compound with picric acid, which, when pure, melts at 118·2° (corr.)

2. *Oxidation by Nitric Acid.*—The resin is gradually added to strong nitric acid contained in a flask surrounded by ice. When the reaction has moderated, the liquid is warmed. On concentrating the liquid, and then allowing it to cool, it deposits a pale yellow crystalline powder; this when purified by crystallisation from water, is obtained in white needles, which were shown to consist of isophthalic acid.

3. *Action of Fused Potash.*—The resin was prepared by decomposing absolute aldehyde, which was diluted with its own volume of absolute alcohol, and placed in a freezing mixture, with an excess of a concentrated alcoholic solution of potash. The liquid was allowed to stand 24 hours, and then heated at 100° with an inverted condenser. The resin is then fused with potash, and treated with ether in the usual way; the semi-solid mass thus obtained was found to consist of α -hydroxyisophthalic acid (m. p. 283—284°), metahomosalicylic acid, or hydroxytoluic acid, $C_8H_8O_3$ (m. p. 173°), and metaxyleneol, $C_8H_{10}O$. On fusing the phenol with potash, the same mixture of acids was obtained as when the resin was fused with potash, namely α -hydroxyisophthalic acid, and metahomosalicylic acid (hydroxytoluic).

J. I. W.

Action of Aldehyde on Furfuraldehyde. By J. G. SCHMIDT (*Ber.*, **13**, 2342—2345).—*Furfuracrolein*, $C_7H_6O_2$, is formed by heating at 60° furfuraldehyde (1 part) and aldehyde or paraldehyde (2 parts) with a dilute solution of soda. When the mixture assumes a brown colour and begins to thicken, it is neutralised with tartaric acid and distilled. The distillate is extracted with ether, and the extract dis-

tilled until the temperature rises to 210° . The residue in the retort is cooled down, pressed between bibulous paper, and recrystallised from hot water, when the furfuracrolein is obtained in almost colourless needles (m. p. 51°), soluble in alcohol, ether, and hot water. It is volatile in a current of steam, and boils at 200° with partial decomposition. Treatment with silver oxide converts it into furfuracrylic acid, previously described by Baeyer (this Journal, 1877, ii, 444).

Furfuracrolein is also formed in small quantities when hydrochloric acid is passed through a solution of paraldehyde and furfuraldehyde in chloroform. W. C. W.

Transformation of Chloral into Metachloral. By H. BYASSON (*Compt. rend.*, **91**, 1071).—The author has found that when anhydrous chloral is freed from all traces of sulphuric acid, the liquid will remain without change, whether kept in the dark or exposed to light, for at least four years. Caustic baryta is used to remove the sulphuric acid; the liquid is then decanted and redistilled. R. R.

Symmetrical β -Dichloracetone. By J. HOERMANN (*Ber.*, **13**, 1706—1709).—This is a reply to Kolbe (*J. pr. Chem.*, **22**, 105), who claims for Glutz and Fischer (*ibid.*, **4**, 55) the discovery of this compound. The author points out that its discovery is due to Markownikoff (*Ber.*, **4**, 562), who later (*Ber.*, **6**, 1210) describes it as a solid melting at 43° . The author prepares β -dichloracetone by heating dichlorhydrin at its boiling point, with potassium dichromate and sulphuric acid. A violent reaction takes place, and the dichloracetone and unaltered dichlorhydrin distil over; the former is separated by converting it into the solid compound with sodium hydrogen sulphate, which when decomposed with dilute sulphuric yields β -dichloracetone, when it has the properties assigned to it by Markownikoff.

The author concludes that the liquid β -dichloracetone described by Glutz and Fischer consisted of a mixture of dichlorhydrin with the dichloracetone, as dichloracetone when pure solidifies easily. Amongst the products of the oxidation of dichlorhydrin are monochloracetic acid and formic acid, carbonic anhydride being evolved during the reaction. P. P. B.

Action of Bromine on Acetic Anhydride, Acetic Bromide, Ethyl Acetate, Ethyl Succinate, Isobutyl Isobutyrate, and Succinic Acid. By F. URECH (*Ber.*, **13**, 1687—1696).—The author has carefully studied the phenomena presented by the action of bromine on the above-named compounds, and has determined the percentage of bromine entering into combination at varying intervals of time, and at different temperatures. P. P. B.

Conversion of Chlorocarbonic Acid into Formic Acid. By A. GEUTHER (*Annalen*, **205**, 223—226).—The four affinities of carbon can in its oxygen-compounds be separated into two groups of two affinities each. In the first group are the two affinities of oxygen in carbonic oxide; in the second group are the two further affinities which come into action in the conversion of carbonic oxide into

carbonic anhydride. The former might be called "carbonic oxide affinities," the latter "carbonic anhydride affinities." The author with Röse (*vide* next abstract) proposes to answer these questions: 1st. Are the carbonic anhydride affinities equal or unequal? 2nd. Are the carbonic oxide affinities equal or unequal? 3rd. Are the carbonic anhydride and carbonic oxide affinities equal or unequal? Carbon oxychloride and the ethers derived therefrom is made the starting point, and the author investigates as to whether it is possible to replace the chlorine by hydrogen, and convert chlorocarbonic into formic acid, and whether the acid obtained is identical or not with ordinary formic acid. This conversion was formerly attempted by Butlerow (*Zeitsch. f. Chem.*, 1863, 489), but with unsatisfactory results. The author finds, however, that by the action of sodium-amalgam and water on ethyl chlorocarbonate, an ether of formic acid is obtained; and that the *lower* the temperature, and the *longer* the time, the greater the yield of formic acid.

The crude products of the reaction were distilled with excess of tartaric acid, and the acid distilling over was found to be identical with ordinary formic acid. Three experiments are quoted: in the first an insufficient quantity of sodium-amalgam was used, and the yield of formic acid was 34 per cent. of the theoretical quantity; in the second, with a sufficient quantity of sodium-amalgam and the flask cooled with water, the yield of formic acid was 40 per cent.; in the third the flask was cooled with ice, and the yield 51 per cent. V. H. V.

Conversion of Ethyl Acetate into Butyric Acid. By LUBAVIN (*Bull. Soc. Chim.* [2], 34, 679).—When ethyl acetate is heated with lime in sealed tubes at 250–280°, the principal product is butyric acid. According to the author, an acetate and an ethylate are first formed, thus: $2\text{CaO} + 2\text{C}_4\text{H}_8\text{O}_2 = (\text{C}_2\text{H}_3\text{O}_2)_2\text{Ca} + (\text{C}_2\text{H}_5\text{O})_2\text{Ca}$, and these react in accordance with the equation $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Ca} + (\text{C}_2\text{H}_5\text{O})_2\text{Ca} = (\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca} + \text{CaH}_2\text{O}_2$. C. H. B.

Occurrence of a Fatty Acid in the Paraffin of Beech-wood Tar. By C. HELL (*Ber.*, 13, 1709–1713).—In the dry distillation of beech-wood, a paraffin-like body condenses in the receiver next the retort; from this the author has obtained a paraffin, m. p. 44–45°, identical with Reichenbach's paraffin; also an acid which is separated from the former by its greater solubility in alcohol. This acid, the author styles *lignoceric acid* (see next abstract). The acid is accompanied by an alcohol, which together make up about 10 per cent. of the raw material. P. P. B.

Lignoceric Acid. By C. HELL and O. HERMANN (*Ber.*, 13, 1713–1721).—This acid was separated from beech-wood paraffin by extracting the latter with boiling alcohol; the acid is deposited from its alcoholic solution on cooling, and after recrystallising from light petroleum, melts at 75°. It is then freed from an alcohol which accompanies it by converting it into the sodium salt, and recrystallising this from light petroleum and alcohol.

The acid obtained from the sodium salt melts at 79°, forming a brown liquid, which solidifies to a crystalline leafy mass.

The best method for obtaining the acid pure is to convert the crude acid (m. p. 75°) into the *methyl salt*, which after crystallisation from light petroleum, is obtained in white, lustrous, acuminate leaflets. It is soluble in cold chloroform or carbon bisulphide, and less soluble in other solvents; it melts at $56.5-57^{\circ}$, and distils without decomposition.

The *ethyl salt* resembles the methyl salt in its properties, and melts at 55° ; when distilled, however, it decomposes, the distillate consisting of a mixture of acid, ethyl salt, and Reichenbach's paraffin (m. p. $43-44^{\circ}$); and the residue of free acid, some of the paraffin, and a ketone derived from the acid. At the same time, carbonic anhydride and ethylene are formed.

The acid prepared from the methyl or ethyl salt is perfectly white; it crystallises from light petroleum in crystalline grains, from alcohol in fine needles (m. p. 80.5°). Benzene, carbon bisulphide, glacial acetic acid, and chloroform dissolve it when heated, and deposit it on cooling. Analyses of the acid and of its salts show its formula to be $C_{23}H_{47}.COOH$. It, therefore, occupies a position between behenic and cerotic acids.

Sodium lignocerate, $C_{23}H_{47}.COONa$, is a light white powder, soluble in absolute alcohol and is decomposed above 200° . *Copper lignocerate* ($C_{23}H_{47}.COO$) $_2Cu$, is a bluish-green powder, obtained by precipitating the alcoholic solution of the sodium salt with copper acetate. When heated, it first melts to a bluish-green liquid, and then decomposes. It is soluble in benzene, but insoluble in alcohol, ether, and light petroleum. *Lead lignocerate* ($C_{23}H_{47}.COO$) $_2Pb$, obtained as a white powder (m. p. 117°), behaves with solvents like the copper salt. *Silver lignocerate*, $C_{23}H_{47}.COOAg$, is obtained as a white precipitate, not much affected by light; it appears to melt about 155° , and is decomposed above 200° . With solvents, it behaves like the copper and lead salts. *Potassium lignocerate*, $C_{23}H_{47}.COOK$, crystallises from absolute alcohol, as a white powder which, with water, forms a gelatinous soap. It does not melt at 190° , and is decomposed at higher temperatures. *Lignoceric chloride*, $C_{23}H_{47}.COCl$, is obtained by acting on the free acid with phosphorus pentachloride, and expelling the phosphorus oxychloride by a current of dry air. The residue crystallises from pure ether as a slightly yellow leafy mass, m. p. $48-50^{\circ}$. It is soluble in light petroleum, and is converted into an amide by ammonia.

In the distillation of brown coal, a similar acid is obtained, viz., *geoceric acid*, $C_{26}H_{52}O_2$. P. P. B.

Polymerides of Methyl Acrylate. By G. W. A. KAHLBAUM (*Ber.*, **13**, 2348—2351).—On exposure to the light, methyl acrylate slowly changes into a transparent gelatinous modification which is insoluble in alcohol, ether, water, inorganic acids, and alkalis.

On distilling this compound under 115 mm. pressure, a liquid polymeride is obtained, which boils at 190° under 100 mm. pressure.

The sp. gr. and index of refraction at 20° of these three modifications was determined.

	Sp. gr.	Index of refraction for Na line.	Specific refraction.
Methyl acrylate	0.960	1.3984	0.4150
Liquid product.	1.123	1.4600	0.4090
Solid product	1.222	1.4725	0.3866

W. C. W.

Preparation of Glycollic Acid from Sugar. By H. KILLIANI (*Annalen*, 205, 191—193).—Levulose, dextrose, and starch-sugar at ordinary temperatures or at 50—55° C. are easily oxidised by silver oxide into glycollic, oxalic, and carbonic acids.

At a temperature of 100° only a small quantity of glycollic acid is formed.

The author obtained the following results at ordinary temperatures: from dextrose, 41.5—47.4 per cent.; from levulose, 20.37—22.1 per cent.; and from starch-sugar, 25.8 per cent. of the theoretical quantity of glycollic acid.

At a temperature of 50°, from dextrose, 34 per cent. of glycollic acid, and at the temperature of the water-bath from levulose, 19—24 per cent., and from dextrose 8.98—9.79 per cent. of glycollic acid. This process is recommended as an economical and ready method of obtaining pure glycollic acid.

V. H. V.

Methyl Carbonate. By C. COUNCLER (*Ber.*, 13, 1697—1699).—This compound can be prepared in a manner similar to amyl carbonate (Medlock, *Annalen*, 69, 217), viz., by heating methyl chlorocarbonate with lead oxide in a vessel attached to a reversed condenser. Methyl carbonate, Me_2CO_3 , resembles the ethyl salt, has a sp. gr. 1.069 at 22°, and boils at 92.97°. It burns, and is miscible with alcohol, methyl alcohol and chloroform.

Trichloromethane carbonate $(\text{CCl}_3)_2\text{CO}_3$, is obtained by the action of chlorine on the methyl salt in sunlight; it is a solid which melts to a liquid and solidifies at 78—79°. It is volatile at the ordinary temperatures, and attacks the mucous membrane; it may be recrystallised from ether. In many of its properties, it resembles pentachloroethane carbonate, from which it differs in being undecomposed by distillation under the ordinary pressure. It is partially decomposed when heated in sealed tubes to 200°.

P. P. B.

Ethereal Salts of Carbonic Acid. By B. RÖSE (*Annalen*, 205, 227—254).—If in carbon oxychloride both the affinities of the carbon-atom with the chlorine-atoms are equal, then by the action of an alcohol on it, both the chlorine-atoms should equally be replaced by alcoholic groups. An intermediate chlorocarbonic ether, however, is always obtained, and would indicate an inequality of the affinities of the carbon-atoms. The author has investigated the ethereal salts of carbonic acid, in order to decide on the equality or inequality of the carbon-atom affinities.

PART I.—Chlorocarbonic Ethers. By the action of alcohols on carbon oxychloride, the following chlorocarbonic ethers were obtained:—

	Boiling point.	Specific gravity.
Methyl chlorocarbonate	71.4	1.236
Propyl " 	115.2	1.094
Isobutyl " 	128.8	1.053
Isopentyl " 	154.3	1.032

The author considers that Römer's researches (*Ber.*, 6, 1101) on the propyl, and those of Mylius (*Ber.*, 5, 972) on the isobutyl chlorocarbonate, were incorrect.

PART II.—(1.) *Simple Ethereal Salts of Carbonic Acid, those having the same Alcohol Radical.*—By the action of the alcohols or sodium alcoholates on the chlorocarbonates, the author has prepared and investigated the following ethers:—

	Boiling point.	Sp. gr.	Index of refraction.
Dimethyl carbonate....	90.6	1.065	1.3748
Dipropyl " 	168.2	0.949	1.3986
Diisobutyl " 	190.3	0.919	1.4048
Diisopentyl " 	228.7	0.912	1.4153

(2.) *Mixed Ethereal Salts of Carbonic Acid or those having Different Alcohol Radicals.*—If the affinities of the chlorine-atom and the alcoholic group to the carbon-atom in the chlorocarbonic ethers are different, then the mixed ethereal salts formed by the action of ethyl alcohol on methyl chlorocarbonate and of methyl alcohol on ethyl chlorocarbonate respectively will be isomeric, and not identical. To decide this point, the actions of methyl, ethyl, and propyl alcohols on methyl, ethyl, and propyl carbonates were investigated. The reaction effected at ordinary temperatures gave, on fractionally distilling the products, the following results:—

Ethyl alcohol and methyl chlorocarbonate gave diethyl carbonate.

Propyl	"	"	"	dipropyl	"
Methyl	"	ethyl	"	"	ethyl-methyl carbonate
Propyl	"	"	"	"	dipropyl "
Methyl	"	propyl	"	"	methyl-propyl "
Ethyl	"	"	"	"	ethyl-propyl "

But as in some of these reactions, instead of the mixed ethereal salts, the simple dibasic salts are formed, it appears that the more complex alcoholic group displaces from a mixed ether the less complex alcoholic group. To confirm this, the author acted on methyl propyl carbonate with propyl alcohol, and obtained dipropyl carbonate and methyl alcohol. It is only when the alcohols act on the chlorocarbonic ethers at low temperatures (6—8°) that the mixed ethereal salts are obtained. Adopting this precaution, the following reactions were investigated:—Ethyl, propyl, and isobutyl alcohols on methyl chlorocarbonate, isobutyl and isoamyl alcohols on ethyl chlorocarbonate, methyl and ethyl alcohols on isobutyl chlorocarbonate, and ethyl alcohol on isoamyl chlorocarbonate. By these experiments it was established that the *mixed ethereal salts of carbonic acid containing identical alcohol groups, by whatever method they are prepared, are iden-*

tical. Hence the carbon affinities, which combine with alcoholic groups in the ethereal salts (as the chlorine atoms in carbon oxychloride), are equal.

Properties of Mixed Ethers.

	Boiling point.	Sp. gr.	Index of refraction.
Methyl-ethyl carbonate. . .	109.2	1.002	1.377
Methyl-propyl „ . . .	130.8	0.978	1.386
Methyl-isobutyl „ . . .	143.6	0.951	1.3922
Ethyl-isobutyl „ . . .	160.1	0.931	1.3965
Ethyl-isopentyl „ . . .	182.3	0.924	1.4053

(3.) *Action of Phosphorus Pentachloride on the Ethereal Salts of Carbonic Acid.*—Geuther has observed that ethyl chlorocarbonate and ethyl chloride are formed by the action of phosphorus pentachloride on diethyl carbonate. The author shows that by the action of phosphorus pentachloride on ethyl-isopentyl carbonate, isopentyl chlorocarbonate and ethyl chloride are produced, the more complex group remaining in combination with the carbon-atom, whilst the less complex group is replaced by chlorine. This reaction gives a means for determining whether any given ethereal salt is simple or mixed.

PART III.—*Ethereal Salts of Tetrabasic Carbonic Acid.*—The action of various sodium alcoholates on chloropicrin was studied, and the following orthocarbonic ethers analogous to Bassett's orthoethyl carbonate are described;—

	Boiling point.	Sp. gr.
Orthopropyl carbonate.	224.2	0.911
Orthoisobutyl „	244.9	0.900

But by the action of dry sodium methylate on chloropicrin, neither the ether of tetrabasic nor of dibasic carbonic acid was formed; so that it does not seem that orthomethyl carbonate exists. V. H. V.

Anhydride and Ethers of Isodibromosuccinic Acid. By A. PICTET (*Ber.*, **13**, 1669—1671).—Isodibromosuccinic acid is obtained by heating maleic acid with bromine; at the same time, some dibromosuccinic acid is formed, owing to a partial conversion of the maleic into fumaric acid. This loss of maleic acid may be avoided by acting on maleic anhydride with bromine, whereby *isodibromosuccinic anhydride*, $C_2H_2Br_2 \cdot C_2O_3$, alone is formed. It may be prepared by dissolving maleic anhydride in dry chloroform, and heating it in sealed tubes with bromine at 100° . After expelling the chloroform on a water-bath, isodibromosuccinic anhydride is obtained as an oil; it takes up water very quickly, being converted into isodibromosuccinic acid. The anhydride can be kept in sealed tubes only; on cooling it solidifies, forming colourless tabular crystals (m. p. 32°). Isodibromosuccinic anhydride is very unstable; at 100° it yields hydrobromic acid and bromomaleic anhydride (b. p. 214°), which takes up water, forming monobromomaleic acid (m. p. 127 — 128°).

Kekulé (*Annalen*, Sup., **2**, 85), by the action of bromine on maleic anhydride at 100° , obtained a liquid, which was allowed to crystallise

in an exsiccator, and was evidently a mixture of isodibromosuccinic acid and the anhydride.

The properties of isodibromosuccinic acid, prepared from the anhydride obtained as above, are identical with those described by Fittig and Petro (this Journal, **36**, 372).

Methyl and *ethyl isodibromosuccinates*, obtained in the usual manner from isodibromosuccinic acid, are oily liquids, which decompose on heating.
P. P. B.

Oxyethylidenesuccinic Acid. By C. BÖTTINGER (*Ber.*, **14**, 148 150).—When oxyethylidenesuccinamic acid is boiled for several hours (in an atmosphere free from carbonic anhydride) with a slightly larger quantity of baryta-water than is required for the formation of a neutral salt, *barium methyltartronate* or *oxyethylidenesuccinate* is deposited as a dense white crystalline precipitate, soluble in ammonium chloride. Methyltartronic acid crystallises in rhombohedra, resembling calcspar. When cautiously heated, it melts at 178° with copious evolution of carbonic anhydride; the melting point is lower if the heat is applied suddenly. A neutral solution of the ammonium salt produces white crystalline precipitates with the silver nitrate, lead and zinc acetates, and with hot solutions of calcium chloride and barium acetate. Oxyethylidenesuccinamic acid is decomposed by boiling with strong hydrochloric acid, yielding fermentation lactic acid and carbonic anhydride.
W. C. W.

Formulæ of Maleic and Fumaric Acids. By H. HÜBNER (*Ber.*, **14**, 210).—The author explains that he accepts Kekulé's views concerning the constitution of maleic and fumaric acids, and that he does not consider that the former acid has been conclusively proved to

—CH.COOH
have the formula $\begin{array}{c} | \\ \text{—CH.COOH} \end{array}$

W. C. W.

Action of Ammonia on Ethyl Chloromaleate. By A. CLAUS and F. VOELLER (*Ber.*, **14**, 150—153).—Alcoholic ammonia acts on ethyl chloromaleate at the ordinary temperature. If molecular proportions of ammonia and the ethyl salt are taken, ethyl chloromaleamate is obtained in anhydrous rhombic crystals (m. p. 102°). By the action of 2 mols. of ammonia on ethyl chloromaleate, a mixture of *ethyl amidomaleate* (m. p. 100°) and *amidomaleamate* is produced. Ethyl chloromaleate is completely converted into ethyl amidomaleamate by treatment with 3 mols. of ammonia. This compound is deposited from an alcoholic solution in transparent prisms (m. p. 62°), soluble in ether. If 4 mols. of ammonia are employed, the diamide of amidomaleic acid is obtained in colourless scales (m. p. 122°), which are soluble in alcohol, ether, and hot water. Amidomaleic acid, derived from either of the three last-mentioned compounds by saponification, forms a deliquescent crystalline mass (m. p. 180°). When the silver salt of this acid is heated, it explodes.

By treating ethyl chloromaleamate with alcoholic soda, sodium amidomaleamate is produced.
W. C. W.

Tetrollic and Oxytetrollic Acids and their Homologues.

By E. DEMARÇAY (*Bull. Soc. Chim.* [2], **33**, 575—580).—This is a continuation of a paper (*Bull. Soc. Chim.* [2], **33**, 516) already abstracted in this Journal (1880, Abstr., 625).

Pentolic acid, $\text{H}_2\text{O} \cdot 3\text{C}_5\text{H}_8\text{O}_2$, is prepared from ethylic ethylacetate in a manner precisely similar to tetrollic acid (*loc. cit.*). The finest crystals are obtained by slow evaporation of its aqueous solutions; they are orthorhombic, and have three planes of cleavage. It melts at 128° , and is less soluble in cold water than tetrollic acid, but very easily in boiling water, alcohol, or ether. The *calcium salt*, $2\text{CaO} \cdot 5\text{C}_5\text{H}_8\text{O}_2 + 2\text{H}_2\text{O}$, is very soluble in water, as is also the *barium salt*, $\text{BaO} \cdot 2\text{C}_5\text{H}_8\text{O}_2$. Pentolic acid gives a violet coloration with ferric chloride; fused with potash, it yields a mixture of formate and butyrate. It gives a nitro-derivative with nitric acid, and with phosphorus pentachloride the *chloride* $\text{C}_5\text{H}_6\text{Cl}_2\text{O}$ (b. p. $189\text{--}191^\circ$).

Hexolic acid, $\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_8\text{O}_2$, obtained from ethylic propylacetate, crystallises in large iridescent plates (m. p. 126°), less soluble in water, and more soluble in chloroform than pentolic acid. Fused with potash, it yields a formate and valerate.

Isohexolic acid, $\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_8\text{O}_2$, obtained from ethylic isopropylacetate, melts at 124° . It closely resembles the other members of the group in its general characters.

Heptolic acid, $\text{H}_2\text{O} \cdot 3\text{C}_7\text{H}_{10}\text{O}_2$.—The only heptolic acid prepared was the one from ethyl isobutylacetate. It crystallises in long flattened needles (m. p. $150\text{--}151^\circ$), resembling benzoic acid in appearance. It is but very sparingly soluble in cold water; the barium salt is very soluble.

Oxytetrollic acid, $3\text{C}_4\text{H}_4\text{O}_3 \cdot \text{H}_2\text{O}$.—The method of preparing this is described in the previous paper (*loc. cit.*, p. 520). The ethylic methylacetate, mixed with a little water, is treated with 2 mols. of bromine, half of which is added gradually, keeping cool, and then the second half at once. When decolorised, it is precipitated by water, decomposed with alcoholic potash, and after removal of the alcohol, acidified with hydrochloric acid. The acid is extracted by agitation with ether, and after purification by treatment with chloroform and crystallisation from water, forms nodular masses, consisting of microscopic needles (m. p. $203\text{--}204^\circ$). It boils at about 280° , with partial decomposition. It is very soluble in alcohol, ether, and boiling water, but insoluble in chloroform. It forms well-crystallised salts, several of which are described. Its ethereal salt is an oily liquid, insoluble in water. With phosphorus pentachloride, the *chloride* $\text{C}_4\text{H}_3\text{Cl}_3\text{O}$ is formed, which is reconverted into oxytetrollic acid by water, and yields the *ethereal salt*, $\text{C}_4\text{H}_3\text{O}(\text{EtO})_3$, with alcohol. This ethereal salt is a limpid, slightly viscous liquid (b. p. 225°), of feeble aromatic odour. Aqueous ammonia converts it into the *amide* of oxytetrollic acid, $\text{C}_{12}\text{H}_9\text{O}_5(\text{NH}_2)_3$, which is also obtained from the chloride $\text{C}_4\text{H}_3\text{Cl}_3\text{O}$ by the action of ammonia; it crystallises in plates (m. p. 177°). If the chloride is poured into a large quantity of alcohol and aqueous ammonia is then added, the amidated compound $\text{C}_4\text{H}_3\text{O}(\text{EtO})_2 \cdot \text{NH}_2$ is formed; it crystallises in lustrous plates (m. p. $68\text{--}69^\circ$), which are decomposed by prolonged boiling with water, ammonia being dis-

engaged. The action of zinc and dilute sulphuric acid converts oxytetrolic acid into *hydroxytetrolic acid*, $C_4H_5O_3$, which may be extracted from the solution by agitation with ether. It forms a crystalline mass (m. p. 111°), very soluble in water, alcohol, or ether. It forms salts of the general formula $C_4H_5O_3M' + C_4H_4O_3M'_2$, several of which are described. The ethereal salt is an oil of aromatic odour, insoluble in water. C. E. G.

Tartronic Acid produced by the Oxidation of Glycerol with Potassium Permanganate. By G. CAMPANI and D. BIZZARRI (*Gazzetta*, 10, 489—491).—Tartronic acid is known to be produced by the action of nitric acid on glycerol, and the author finds that potassium permanganate also gives rise to the same acid, but the operation has to be carefully conducted. Pure glycerol of sp. gr. 1.25 is mixed with an equal bulk of water, and finely powdered permanganate and small quantities of water are gradually added, filtering at intervals, and taking care to avoid rise of temperature. When permanganate equal to half the weight of the glycerol has been added, the operation is stopped, the clear liquid concentrated in a vacuum, neutralised with acetic acid, and precipitated with lead acetate. This precipitate consists of lead oxalate and tartronate. The tartronic acid, after separation of the oxalic acid, crystallises in long colourless prisms (m. p. about 160°), very soluble in alcohol and in water. The acid gives no precipitate with barium or calcium chloride. The barium salt was found to have the composition expressed by the formula $C_3H_2BaO_5$. C. E. G.

Dioxyadipic Acid. By E. HJELT (*Ber.*, 14, 144—145).—Barium dioxyadipate, $C_6H_5O_6Ba$, is formed when dibromallymalonic acid is treated with baryta. An aqueous solution of dioxyadipic acid is stable at the ordinary temperature, but undergoes partial decomposition at 100° , losing a molecule of water, and forming a monobasic acid. By the action of baryta-water on the monobasic acid, barium dioxyadipate is again produced. W. C. W.

Fermentation of Tartaric Acid. By F. KÖNIG (*Ber.*, 14, 211—217).—The chief product of the action of bacteria on a neutral solution of ammonium tartrate containing small quantities of potassium phosphate, magnesium sulphate, and calcium chloride, is succinic acid. Acetic, carbonic, and occasionally formic acid, are also produced. Under similar conditions, calcium tartrate yields acetic and carbonic acids, together with small quantities of formic, propionic, and butyric acids. W. C. W.

Synthesis of Citric Acid. By A. KEKULÉ (*Ber.*, 13, 1686—1687).—In this preliminary notice the author, after referring to the investigations of Grimanx and Adam (this Journal, 38, 801), and of Andreoni (*Ber.*, 13, 1394), states that he has obtained an acid giving some of the reactions of citric acid, in the following manner:—An ethereal solution of diethyl acetoxy malate is acted on by sodium, the product is then treated with ethyl bromacetate. The triethyl salt so obtained was then saponified with potash, and the lead salt of the acid prepared ;

on decomposing this with hydrogen sulphide, an acid was obtained showing some of the reactions of citric acid. P. P. B.

Carbamidacetosulphonic Acid, a New Derivative of Thiohydantoin. By R. ANDREASCH (*Wien. Akad. Ber.* [2 Abth.], **81**, 978—987).—An abstract of this paper appeared in this Journal, **38**, 877). It may be added that if the experiment is not conducted exactly as described by the author, very little or even no potassium carbamidacetosulphonate is formed. He added the 4.2 grams of finely powdered potassium chlorate, a fifth part at a time, to the 5 grams of thiohydantoin, and 50 c.c. hydrochloric acid, sp. gr. 1.08, the action being allowed to subside before each fresh addition; the temperature was prevented from rising too high, and the reaction was kept going by alternately cooling or warming. There was no perceptible evolution of chlorine.

NOTE.—In the *Berichte* abstract the word “Chlorentwicklung” has been substituted for “Wärmeentwicklung.” D. A. L.

Multiples in the Optical Rotatory Power of Organic Compounds. By T. THOMSEN (*Ber.*, **13**, 2269—2272).—The molecular rotatory power of the mannitol derivatives is a multiple of 22.8. The constant 3.8 will consequently be common to both the carbohydrate and mannitol compounds. The alcoholic amides, however, have the constant 8.5°, viz.:—

	$\frac{m[\alpha]_D}{100}$	
Aspartic acid	33.4	= 4 × 8.35
Asparagine	41.2	= 5 × 8.24
Glutamic acid	51.0	= 6 × 8.50
Sodium glycocholate ..	101.2	= 12 × 8.43
Glycocholic acid	134.55	= 16 × 8.43

W. C. W.

Inversion of the Rotation of Optically Active Substances. By H. LANDOLT (*Ber.*, **13**, 2329—2339).—The rotatory power of an aqueous solution of tartaric acid is diminished by the addition of acids. Solutions in methyl or ethyl alcohol and in acetone are almost inactive. If the tartaric acid is dissolved in a mixture of dry acetone and ether, or in anhydrous acetone and chloroform, it is feebly lævogyrate. Schneider (*Ber.*, **13**, 620, this Journal, 1880, Abstr., 629) has shown that a solution containing 32.42 per cent. of malic acid is optically inactive, whilst stronger solutions are dextrogyrate, and weaker solution lævogyrate. The rotatory power of asparagine and aspartic acid is inverted by the addition of acetic acid.

Molecules of		Water.	α_D at 20°.
Asparagine.	Acetic acid.		
1	1	300	— 3·52°
1	2	300	— 3·12
1	7	300	— 0·58
1	10	300	0
1	15	300	+ 1·13
1	20	300	+ 2·70
Aspartic acid.			
1	1	284·4	— 3·11
1	3	284·4	— 0·38
1	4	284·4	— 0·12
1	5	284·4	+ 0·18
1	10	284·4	+ 1·74

An aqueous solution of invert sugar becomes optically inactive at a temperature of 87·2°; the alcoholic solution is optically inactive at 38°. Racemic acid is inactive at 80°. Mannitol in dilute aqueous solution is feebly lævogyrates; the addition of an alkali increases its optical activity, whilst borax inverts it.

All optically active organic compounds contain an asymmetric carbon-atom.

W. C. W.

Cyanamido-compounds of Succinic Acid. By H. MÖLLER (*J. pr. Chem.*, [2], **22**, 193—223) —As Mertens has shown (*ibid.*, **17**, 1) that some of the cyanamido-compounds of monobasic acids bore a close resemblance to cyanamide, the author was induced to investigate the nature of the corresponding compounds of the dibasic acids.

Potassium Succinocyanate, $\text{COOK} \cdot \text{C}_2\text{H}_4 \cdot \text{CO} \cdot \text{NK} \cdot \text{CN} + \text{H}_2\text{O}$.—Succinic anhydride, prepared by distilling a mixture of succinic acid with succinic chloride, is gradually added to a solution of potassium cyanamide in alcohol, and the precipitate which is formed collected and washed with alcohol. It may be purified by repeatedly dissolving in water, and reprecipitating with alcohol. A good result is also obtained when the anhydride is added to an aqueous solution of potassium cyanamide, the potassium succinocyanate being precipitated by adding alcohol and cooling strongly. It crystallises in rhombic plates, easily soluble in water, but insoluble in alcohol. *Sodium succinocyanate* cannot be obtained in the pure state directly from sodium cyanamide and succinic anhydride, but may be prepared from the silver salt by the action of sodium chloride; it is even more soluble in water than the potassium salt, and crystallises in large, sword-shaped plates, containing $5\text{H}_2\text{O}$. The *calcium salt*, prepared like the sodium salt, crystallises with $4\text{H}_2\text{O}$ in tufts of long narrow plates. The *barium salt* may be prepared directly by adding baryta-water to succinic anhydride suspended in an aqueous solution of cyanamide until alkaline, boiling, and filtering. On adding alcohol, the succinocyanate separates out in tufts of rhombic prisms, containing $2\text{H}_2\text{O}$. It is more easily soluble in water than the potassium compound, and the aqueous solution is easily decomposed. To prepare the pure *silver salt*, the crude

potassium succinocyanate is dissolved in water, ammonia and barium nitrate added, and the solution heated to boiling. On cooling, the barium succinate is removed by filtration, nitrate of silver added, and the precipitate of silver succinocyanate dissolved by ammonia; on filtering from undissolved silver cyanide, and neutralising with nitric acid, pure silver succinocyanate is thrown down. It is easily soluble, both in ammonia and in dilute nitric acid. When silver nitrate is added to a solution of succinocyanic acid, oily drops separate, which become crystalline on standing, this is an *acid succinocyanate of silver*. It is but sparingly soluble in dilute nitric acid. *Succinocyanic acid*, $\text{COOH.C}_2\text{H}_4\text{CO.NH.CN}$, may be obtained from the silver salt by suspending it in dry pure ether, and decomposing it with hydrogen sulphide; on evaporating, the acid is left in the crystalline state. It is very soluble in water, and also in alcohol or ether, crystallising out on evaporation in tufts of lancet-shaped plates (m. p. 128°). It decomposes rapidly in aqueous solution. The normal salts of the metals are insoluble.

Succinocyanimide, $\text{C}_2\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{N.CN}$, is formed on digesting succinic chloride with excess of cyanamide in ethereal solution. When all the chloride is decomposed, the ethereal solution is evaporated, and the residue after being washed with water to remove cyanamide and cyanamide hydrochloride, is crystallised from boiling alcohol in which it is easily soluble. On cooling, nearly the whole of the succinocyanimide separates out in thin plates resembling naphthalene in appearance (m. p. 138°). When boiled with water it decomposes, yielding succinocyanic acid, whilst long-continued heating with alcohol converts it into *ethyl succinocyanate*, $\text{COOEt.C}_2\text{H}_4\text{CO.NH.CN}$.

The action of ethyl succinate on potassium cyanide in alcohol gives rise to *potassium succinocyanamide*, $\text{C}_2\text{H}_4(\text{CO.NK.CN})_2$, and *sodium succinocyanamide* may be obtained by heating sodium cyanide with succinic chloride in dry alcohol or ether: these compounds, however, could not be separated in the pure state. *Silver succinocyanamide* can be readily prepared from the crude potassium compound by precipitating it with silver nitrate, treating the precipitate with dilute nitric acid to remove silver succinocyanate, and dissolving the residue in ammonia. On pouring the filtered solution into dilute nitric acid, silver succinocyanamide, $\text{C}_2\text{H}_4(\text{CO.NAg.CN})_2 + \frac{1}{2}\text{H}_2\text{O}$, is precipitated in the crystalline state. If it is suspended in alcohol and decomposed by hydrogen sulphide, *succinocyanamide*, $\text{C}_2\text{H}_4(\text{CO.NH.CN})_2 + 2\text{H}_2\text{O}$, is formed, and may be obtained in the crystalline state by allowing the alcoholic solution to evaporate spontaneously. The anhydrous compound melts at $104\text{--}105^\circ$. It resembles cyanamide rather than succinamide. Succinocyanamide is also formed on heating a mixture of cyanamide with succinocyanimide.

C. E. G.

Oxidation of Triethylbenzene. By C. FRIEDEL and M. BALSOHN (*Bull. Soc. Chim.* [2], **34**, 635–638).—When triethylbenzene (b. p. $214\text{--}218$), obtained by the action of ethylene on benzene in presence of aluminium chloride is boiled with chromic mixture, an acid of the composition $\text{C}_{10}\text{H}_8\text{O}_6$ is formed in small quantity. It crystallises in

somewhat large colourless needles, and forms a silver salt crystallising in plates and soluble in warm water. This acid is probably produced by the conversion of two of the ethyl groups into COOH groups, whilst the other ethyl group is converted into acetic acid.

By boiling triethylbenzene for many hours with a large excess of potassium dichromate and sulphuric acid diluted with three times its volume of water, an acid is formed which, in appearance, composition, and the properties of its silver and barium salts corresponds with trimesic acid. By the oxidation of mesitylene with dilute nitric acid, Fittig obtained mesitylenic acid, which when treated with potassium dichromate and sulphuric acid, is converted into trimesic acid. The authors conclude that the acid obtained by the prolonged oxidation of ethylbenzene is mesitylenic acid, and that triethylbenzene is for the most part the symmetrical hydrocarbon analogous to mesitylene.

Ador and Rilliet found that the trimethylbenzene obtained by the action of methyl chloride on benzene in presence of aluminium chloride consisted of mesitylene and pseudocumene. There was no evidence to show that the triethylbenzene obtained by the authors did not contain a substance corresponding with pseudocumene: this latter would be oxidised without giving an aromatic acid.

C. H. B.

Action of Ethylene Bromide on Toluene in Presence of Aluminium Chloride. By C. FRIEDEL and M. BALSOHN (*Bull. Soc. Chim.* [2], **35**, 52—54).—When a mixture of 3 parts ethylene bromide, 15 parts toluene, and 1 part aluminium chloride is gently heated until hydrobromic acid is no longer given off, the product treated with water, and the supernatant oily liquid subjected to fractional distillation, a hydrocarbon (b. p. 297—300°) is obtained, which has the composition $C_{16}H_{18}$, and may be regarded as ditolyethylene, $C_2H_4(C_6H_4.CH_3)_2$.

When oxidised with chromic mixture, it gives isophthalic and terephthalic acids, the former being apparently formed in larger quantity. From this it would appear either that the ditolyethylene obtained consisted of one hydrocarbon, in which the tolyl groups are so arranged that, with reference to the ethylene, one of the methyl groups is in the para-, the other in the meta-position, or that it was a mixture of two isomerides, boiling about the same temperature, in which the two tolyl groups are arranged symmetrically with regard to the ethylene.

C. H. B.

Hexmethylbenzene. By A. W. HOFMANN (*Ber.*, **13**, 1729—1732).—In the preparation of cumidine from xylylidine hydrochloride and methyl alcohol, according to the method of the author and Martius (*Ber.*, **4**, 752), pentamethylaniline, and the hydrocarbon hexmethylbenzene, occur as bye-products. These compounds the author has shown (*Ber.*, **5**, 721) are also formed as bye-products in the action of high temperatures on methylaniline hydrochloride. As cumidine is prepared on the large scale by the above method, the author has been able to obtain large quantities of the bye-products, from which the hexmethylbenzene has been separated.

Hexmethylbenzene, C_6Me_6 , crystallises from alcohol in flat, striated prisms, m. p. 163°, and boils at 253°. Its vapour-density in

aniline vapour was found to be 5.58, theory requiring 5.62. The melting point assigned to this compound differs from that given by Ador and Rilliet (this Journal, **36**, 527).

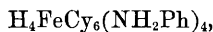
With bromine in sealed tubes at 100°, it yields a compound insoluble in alcohol, but soluble in toluene, and melting at 27°; its formula is apparently $C_{12}H_{18}Br_6$. Oxidising agents act but slowly on the hydrocarbon.
P. P. B.

Oxidation of Di- and Tri-nitrobenzene. By P. HEPP (*Ber.*, **13**, 2346—2348).—A feebly alkaline solution of trinitrobenzene is oxidised to picric acid by potassium ferri-cyanide. Under similar circumstances metadinitrobenzene is converted into a mixture of α - and β -dinitro-phenol.
W. C. W.

Ferrocyanides of Amines. By L. J. EISENBERG (*Annalen*, **205**, 265—272).—The author briefly refers to former literature on the amine ferrocyanides.

Acid Dimethylaniline Ferrocyanide.—Fischer (*Annalen*, **190**, 184; this Journal, 1878, 407) obtained the hydrated salt of acid dimethylaniline ferrocyanide, but owing to its ready decomposition was unable to isolate the anhydrous salt. The author, by dropping a hydrochloric acid solution of dimethylaniline into a solution of potassium ferrocyanide, has succeeded in obtaining the salt in the form of glistening crystals of the composition of $H_4FeCy_6(PhNMe_2)_2 \cdot 2H_2O$. The salt is almost insoluble in cold water, more easily soluble in hot water, but with decomposition; it dissolves readily, however, in hot alcohol without decomposition. The salt is very stable, and can be kept for some time without change.

Neutral Aniline Ferrocyanide.—Kielmayer (*Dingl. polyt. J.*, **214**, 324) obtained this salt in an impure state. The author finds that it cannot be obtained pure by a process similar to that used in the preparation of the above dimethylaniline salt; but by adding excess of aniline to a solution of hydroferrocyanic acid in alcohol, a leafy crystalline precipitate of neutral aniline ferrocyanide,



is obtained. The salt when purified forms pearly crystals easily soluble in cold water, insoluble in cold alcohol and ether. It dissolves easily in hot water, but is decomposed into aniline and hydroferrocyanic acid. When heated, it gives aniline, hydrocyanic acid, and carbide of iron.

Acid Aniline Ferrocyanide.—Fischer (*loc. cit.*) obtained this salt, but was unable to decide its composition. The author by the same process as that used in the preparation of the neutral salt, obtained the acid salt of the formula $FeCy_6H_4(NH_2Ph)_2$.

The author by similar processes obtained *meta*- and *ortho*-toluidine ferrocyanides of the formula $H_4FeCy_6(C_6H_4Me.NH_2)_4$, and *xylylidine ferrocyanide* of the formula $H_4FeCy_6(C_6H_3Me_2.NH_2)$. Experiments with a view of obtaining amide-ferrocyanides and mono- and di-bromaniline ferrocyanides were unsuccessful.
V. H. V.

Action of Primary Aromatic Amines on Acetophenone Bromide. By R. MÖHLAU (*Ber.*, **14**, 171—175).—*Acetophenone anilide*, $\text{Ph.CO.CH}_2\text{.NHPh}$, is formed when acetophenone bromide is dissolved in an equivalent quantity of aniline. The solution quickly solidifies to a crystalline mass, from which aniline hydrobromide is removed by treatment with water. The greater part of the residue dissolves in hot hydrochloric acid, and the acid solution on cooling deposits the hydrochloride in colourless prisms. The free base obtained from the hydrochloride by the action of an alkali crystallises in needles, which are freely soluble in alcohol, ether, benzene, chloroform and carbon bisulphide. The substance melts at 93° , and decomposes when heated above 100° . It is decomposed by boiling with strong hydrochloric acid or potash, forming aniline and phenylcarbylamine.

Phenylisindole is produced when acetophenone anilide or acetophenone bromide is heated with an excess of aniline. After purification by distillation, and by recrystallisation from alcohol, this substance is obtained in lustrous scales (m. p. 185°) insoluble in cold water, but freely soluble in the other ordinary solvents. With an excess of bromine, phenylisindole forms a crystalline compound which melts at 96° with decomposition.

W. C. W.

Action of Nascent Hydrogen on Nitrils. By P. SPICA (*Gazzetta*, **10**, 515).—This is a preliminary notice on the action of nascent hydrogen on benzonitril, being a continuation of the research on the amines corresponding with α -toluic alcohol. The action of zinc and hydrochloric acid on benzonitril in presence of alcohol and water gives rise to *mono*-, *di*- and *tri*-benzylamine, and also ammonia; of these, the first is produced in by far the largest proportion. The melting point of its hydrochloride is 235 — 240° , whilst that of dibenzylamine is 255 — 256° , and of tribenzylamine 227 — 228° . The simultaneous production of primary, secondary, and tertiary amines is analogous to the reaction observed with α -toluic nitril; and shows that the action of reducing agents is not so simple as Mendius supposed. Mendius himself appears to have observed the formation of ammonium chloride (*Annalen*, **121**, 133), but the equation he gives, $\text{C}_n\text{H}_{2n-1}\text{N} + \text{H}_4 = \text{C}_n\text{H}_{2n+1}\text{.NH}_2$, does not account for this.

C. E. G.

Diazo-compounds. By ALEXEJEFF (*Bull. Soc. Chim.* [2], **34**, 684).—When nitrous acid acts on aniline, nitroso-aniline is not obtained, because at the moment of its formation, it reacts with the unaltered aniline, forming diazo-amido-benzene, $\text{NH}_2\text{Ph} + \text{NO.NHPh} = \text{H}_2\text{O} + \text{PhN:N.NHPh}$. According to this hypothesis, diazo-amido-benzene must be regarded as the first term of the reaction, and the salts of diazobenzene must be considered as the products of the transformation of diazo-amido-benzene. From this point of view, the formation of diazo-compounds is analogous to that of azo-compounds. Fischer has shown that the nature of the groups in azo-compounds exercises considerable influence on their stability, and the author considers that the existence of the group N:N in both azo- and diazo-compounds must be admitted.

The author maintains that his method of preparing azo-benzene by

the action of zinc-powder on nitrobenzene is simpler and better than that of Schmidt and Schultz (*Bull. Soc. Chim.*, **32**, 531).

C. H. B.

Existence of Three Isomeric Rosanilines. By A. ROSENSTIEHL (*Bull. Soc. Chim.* [2], **34**, 675—676).—In consequence of the results obtained by E. and O. Fischer, the evidence in favour of the author's supposition that there are three isomeric rosanilines requires revision.

C. H. B.

A Base from Phthalimide. By S. GABRIEL (*Ber.*, **13**, 1684—1686).—When the vapour of phthalimide mixed with hydrogen is passed over heated zinc-dust, a reddish oily distillate is obtained; this is boiled with hydrochloric acid, and after separation of the undissolved oil and resin, the acid solution is supersaturated with soda and distilled in a current of steam. In this way a base is obtained, which crystallises from alcohol in colourless flat rhombs (m. p. 99—100°). From the analysis of the base, of the hydrochloride, and of the platinochloride, its composition appears to be $C_{15}H_{11}N$. Its formation may be expressed as follows:—



The production of ammonia in this reaction has been observed, but the carbonic anhydride is reduced to carbonic oxide by the zinc-dust.

P. P. B.

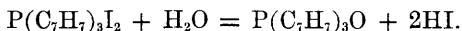
Constitution of Tropine. By A. LADENBURG (*Ber.*, **14**, 227—235).—Hydrotropine iodide, $C_8H_{17}NI_2$, is formed by the action of hydriodic acid and phosphorus on tropine at 140°: if a higher temperature is employed, tropidine and tropidine periodide are produced. Hydrotropine iodide crystallises in colourless prisms. By the action of silver chloride it is converted into a chloriodide, $C_8H_{17}NICl$, which forms crystalline compounds with gold and platinum chlorides: by treatment with silver oxide, it yields a metatropine, $C_8H_{15}NO$, which remains liquid at -30° and boils at 237° .

The compound, $C_8H_{17}NBr_2$, obtained by digesting valerylene bromide with an aqueous solution of trimethylamine is not identical with hydrotropine bromide.

Attempts to prepare tropine or tropidine from piperidine by the action of allyl bromide, allyl iodide, bromallyl alcohol, epichlorhydrin and of glycerol and sulphuric acid, led to negative results.

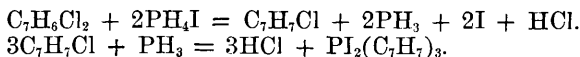
W. C. W.

Tribenzylphosphine Oxide. By F. FLEISSNER (*Ber.*, **13**, 1665—1667).—When benzal chloride heated to 130° is treated with phosphonium iodide in small quantities at a time in an atmosphere of carbonic anhydride, a violent reaction ensues, and a resinous mass is obtained, probably tribenzylphosphine iodide, or a double compound of phosphorus iodide and tribenzylphosphine. The resinous mass is decomposed when heated with water or alcohol, and tribenzylphosphine oxide is obtained: its formation may be expressed as follows:—



t 2

The formation of $P(C_7H_7)_3I_2$, is expressed as follows :—



Tribenzylphosphine oxide, $PO(C_7H_7)_3$, crystallises in white transparent needles (m. p. 213°) soluble in alcohol, ether, benzene, and chloroform. It sublimes without decomposition. It is very stable, and is not acted on by reducing agents, such as hydriodic acid and sulphurous anhydride. It does not combine with acids, but its alcoholic solutions give crystalline double salts with metallic chlorides. The *platinochloride*, $PtCl_4[(C_7H_7)_3PO]_3$, crystallises from alcohol in yellow needles; the *palladiochloride*, $PdCl_2[(C_7H_7)_3PO]_3$, forms a brownish-red mass; the *ferric salt*, $Fe_2Cl_6[(C_7H_7)_3PO]_3$ crystallises in light yellow prisms. The *mercuric salt*, $Hg_2Cl_2[(C_7H_7)_3PO]_3$ forms colourless prisms or pyramids. The *cobalt* compound,



forms blue needles.

P. P. B.

Etherification of Phenols. By V. MERZ and W. WEITH (*Ber.*, **14**, 187—202).—By the action of zinc chloride on phenol at 350° , 5 per cent. of the theoretical yield of diphenyl ether, Ph_2O , is obtained. If aluminium chloride is substituted for zinc chloride, benzene, diphenyl ether, and methylene-diphenyl oxide, $CH_2 < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > O$ are produced. The last-mentioned compound melts at 98.5° , and boils at 315° (corr.). It crystallises in white scales, which dissolve in hot alcohol, acetic acid, and light petroleum. On oxidation, it yields diphenyloxideketone, $CO(C_6H_4)_2O$, a crystalline compound soluble in hot alcohol. The ketone melts at 173° , and boils above 300° . When fused with potash it splits up, forming phenol and salicylic acid.

α -Naphthyl ether, $(C_{10}H_7)_2O$, is formed, together with a small quantity of dinaphthylene oxide, $(C_{10}H_6)_2O$, by the action of zinc chloride or hydrochloric acid gas on boiling α -naphthol. The formation of the dinaphthylene oxide is due to decomposition of α -naphthol by the air in the apparatus. α -Naphthol is decomposed into naphthalene and dinaphthalene oxide by heating in sealed tubes at 350° . α -Naphthyl ether crystallises from alcohol in rhombic plates (m. p. 110°), soluble in benzene, ether, and hot acetic acid. With picric acid, the ethereal solution forms a prismatic compound (m. p. 115°), having the composition $(C_{10}H_7)_2O \cdot 2C_6H_2(NO_2)_3.OH$.

β -Naphthyl ether alone is formed by the action of zinc chloride or dry hydrochloric acid on β -naphthol. It is deposited from hot alcohol in silvery plates (m. p. 105°), soluble in ether, benzene, and hot acetic acid. With picric acid, the ethereal solution forms a crystalline compound (m. p. 122°) resembling the corresponding α -compound.

By long-continued boiling in an apparatus connected with an inverted condenser, or by heating in sealed tubes at 350° , β -naphthol is

converted into β -dinaphthalene oxide $\left| \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \right\rangle O$. This substance crys-

tallises in silvery scales (m. p. 161°), soluble in boiling benzene. The benzene solution forms with picric acid a red crystalline compound (m. p. 170°) having the composition $C_{20}H_{12}O \cdot 2C_6H_2(NO_2)_3OH$.

W. C. W.

Direct Introduction of Carboxyl into Phenols and Aromatic Acids. By C. SENHOFER and C. BRUNNER (*Wien. Akad. Ber.* [2 Abth.], **80**, 504—524; **81**, 430—435 and 1044—1057).—Drechsel (*Zeits. f. Chem.*, 1865, 580) has shown that salicylic acid is produced by the action of potassium bicarbonate on phenol. The authors have examined the behaviour of ammonium carbonate with resorcinol, dihydroxybenzoic acid, orcinol, pyrogallol, and gallic acid.

Part I. When resorcinol is treated at the ordinary temperature with ammonium carbonate for a few days, about 10 per cent. of it is converted into α -dihydroxybenzoic acid, $C_7H_6O_4 + 1\frac{1}{2}H_2O$ (m. p. 194 — 198°), crystallising in needles, readily soluble in alcohol and ether, but sparingly in cold water. Lead acetate gives no precipitate; with ferric chloride a red, and with calcium hypochlorite a violet coloration is produced, becoming brown on adding more hypochlorite. With ammoniacal silver solution, the solution is clear in transmitted, but opaque and grey in reflected light. Alkaline copper solution is not reduced.

Its silver salt, $C_7H_5O_4Ag$, is but little soluble in water; the basic copper compound, $C_7H_4O_4Cu + 2H_2O$, is a yellowish crystalline powder; the normal copper salt, $C_{14}H_{10}O_8Cu + 8H_2O$, crystallises in well-formed emerald-green crystals, and loses 6 mols. H_2O in a vacuum, and 7 mols. H_2O at 100° . Barium α -dihydrobenzoate is readily soluble in water, and crystallises from it in prisms with $4H_2O$. It yields almost the theoretical quantity of resorcinol when heated with powdered pumice-stone. The potassium salt is very easily soluble in water, and separates from it in tufts of needles.

α -Dihydroxybenzoic acid yields a sulphonic acid, the barium salt of which, $C_7H_4O_7S_2Ba + 2H_2O$, crystallises in prisms.

When the treatment of resorcinol with ammonium carbonate takes place at higher temperatures under pressure, an acid of the formula $C_8H_6O_6$ is produced, α -resodicarboxylic acid, differing from Tiemann and Levy's resorcinoldicarboxylic acid. It crystallises in iridescent plates (m. p. 276°), soluble with difficulty in hot water, readily in ether or alcohol. It yields a blood-red coloration with ferric chloride, and neither reduces silver nor copper solutions. The barium salt, $C_8H_4O_6Ba + 5\frac{1}{2}H_2O$, dissolves but little in cold, more readily in hot water: it loses $3H_2O$ at 100° , the rest at 180° . The silver salt, $C_8H_4O_6Ag_2$, is insoluble in water; the copper compound, $C_8H_4O_6Cu + 5\frac{1}{2}H_2O$, crystallises in needles, and loses $4\frac{1}{2}H_2O$ at 100° . The normal potassium salt is most readily soluble in water, from which it crystallises in bundles of needles containing $3H_2O$, whilst the acid potassium compound, $C_8H_5O_6K + H_2O$, is obtained in the form of hard needles.

α -Resodicarboxylic acid dissolves in concentrated sulphuric acid without formation of a sulphonic derivative, and is neither acted on by sodium-amalgam nor by phosphorus pentachloride.

Together with α -resodicarboxylic acid, α -dihydroxybenzoic acid is formed, and a second dihydroxybenzoic acid in small proportion. The last mentioned is readily soluble in hot, much less so in cold water, and with dilute ferric chloride solution gives a purple, with strong solution an intensely blue coloration. It does not act on ammoniacal silver solution, but reduces Fehling's solution at boiling temperature. It loses carbonic anhydride when heated to 135° , and melts at 140° , with formation of resorcinol. Its *silver compound*, $C_7H_5O_4Ag$, forms a crystalline precipitate; the *barium salt* crystallises well in short hard prisms, losing its water of crystallisation (1 mol.) at 160° . The *copper salt*, $C_{14}H_{10}CuO_8 + 8H_2O$, is pale green and crystalline, 7 of the 8 mols. of H_2O being given off at 100° . The *potassium salt* forms soft needles free from water of crystallisation. The *ammonium compound* is similar.

This second dihydroxybenzoic acid is different from that described by Barth and Senhofer, but nearly resembles the hypogallic acid of Matthiessen and Foster, from which it is distinguished by its behaviour with ammoniacal silver solution and with ferric chloride and ammonia, Matthiessen's acid yielding a blood-red, and the authors' acid a light yellow solution.

Only three dihydroxybenzoic acids are possible, and since Barth and Senhofer's acid probably is the 1 : 3 : 5 acid, and the α -acid (first described by M. Ascher) the 1 : 2 : 4, the compound obtained by the authors must be 1 : 2 : 6.

By treating Barth and Senhofer's dihydroxybenzoic acid with ammonium carbonate, β -resodicarboxylic acid is produced, crystallising in four-sided prisms, soluble with difficulty in cold, readily in hot water, without reducing action on silver or copper solutions, furnishing a purple coloration with ferric salts, and crystalline precipitates with calcium and barium chloride; m. p. 250° , with partial decomposition. *Barium β -resodicarboxylate*, $C_8H_4BaO_6 + 4H_2O$, crystallises in white needles. The *acid barium salt* crystallises with $3\frac{1}{2}$ mols. H_2O in long silky needles. A *basic barium salt* has likewise been prepared. The *copper compound* contains $3\frac{1}{2}$ mols. H_2O , of which $1\frac{1}{2}$ are lost at 100° ; the *lead salt* has $1\frac{1}{2}$ mols. H_2O . The *potassium compound* is very readily soluble in water, but little soluble in strong alcohol; *ammonium resodicarboxylate* forms concentric needles, very soluble in water.

The acid when heated with strong sulphuric acid at 130° , dissolves with evolution of carbonic anhydride and formation of a *tetroxy-anthraquinone*, $C_{14}H_8O_6 + 2H_2O$, probably anthrachrysone, a dark green powder.

Part II. Orcinol, treated with ammonium carbonate, yields an acid of the formula $C_8H_5O_4 + H_2O$. It crystallises from dilute alcohol in thin hard needles, melting at 151° , with evolution of carbonic anhydride, and its solution gives a blue coloration with ferric chloride, a white precipitate with silver nitrate and basic lead acetate, and does not reduce alkaline silver or copper solutions; this acid is isomeric with orsellic acid. The authors propose to designate it as *paraorsellic acid*. Heated at about 290° , it is entirely decomposed with reproduction of orcinol. Its *barium compound* is readily soluble in

water, and crystallises from it in four-sided plates, containing 6 mols. H_2O . The *basic barium salt*, $\text{C}_{16}\text{H}_{10}\text{O}_5\text{Ba}_3 + 8\text{H}_2\text{O}$, forms a white crystalline precipitate, becoming reddish on drying. *Copper paraorsellate* is but little soluble in water, and crystallises in needles with 4 mols. H_2O , which are disengaged at 130° . Its solution becomes intensely yellow on adding ammonia, changing to red on standing. The *potassium salt* is readily soluble in water, insoluble in alcohol, and crystallises in long flat anhydrous needles. The *silver* compound is a white insoluble precipitate, the ammonium salt very soluble, and crystallises in well-formed prisms.

Part III. Pyrogallol on treatment with ammonium carbonate yields two acids, readily distinguished by the difference in their solubilities in water, *gallo-carboxylic acid*, $\text{C}_8\text{H}_6\text{O}_7$, and *pyrogallo-carboxylic acid*, $\text{C}_7\text{H}_6\text{O}_8$.

One part of the former dissolves in 2,000 parts of water at 0° ; it is readily soluble in ether and in alcohol, crystallises from water in thin soft needles containing 3 mols. of H_2O . It melts at 270° , but evolves carbonic anhydride below that temperature. It dissolves in hot concentrated sulphuric acid without formation of sulphonic acids. Ferric chloride strikes a purple colour; ferrous salts do not at first produce any coloration, but after some time a dark precipitate separates. The solution heated with calcium carbonate becomes purple, with barium carbonate grey. The acid dissolves in alkalis with brown colour, and precipitates copper, silver, and lead solutions. It does not reduce Fehling's solution, but it becomes bright green. Its *normal barium salt* is but very little soluble in hot or cold water, and forms a crystalline grey precipitate containing 1 mol. H_2O , which it loses at 180° . The *calcium* compound, reddish, flat prisms, is little soluble in cold, easier in hot water, and corresponds with the formula $\text{C}_8\text{H}_4\text{O}_7\text{Ca} + 6\text{H}_2\text{O}$, losing $4\frac{1}{2}$ mols. H_2O at 100° . The *potassium salt* crystallises in thin needles with 2 mols. H_2O , which it loses at 150° .

Pyrogallo-carboxylic acid is isomeric with gallic acid, but is distinguished from it by not yielding rufigallic acid on treatment with strong sulphuric acid. It is readily soluble in alcohol, less so in ether, whilst 1 part of it requires 767 parts of water at 12.5° for solution. With dilute ferric chloride solution it becomes purple, with concentrated brownish-green; with silver nitrate its solution first remains colourless, but gradually reduction takes place. Hypochlorite solution strikes a purple coloration, soon turning brown. Barium and calcium hydrate produce blue precipitates; alkaline copper solution becomes green in the cold, reduced when boiled; ammoniacal silver solution is reduced in the cold. Nitric acid (1.26 sp. gr.) readily decomposes the acid. The solution in strong sulphuric acid becomes purple on the addition of a trace of nitric acid. Its *barium salt* crystallises from water in yellow, hard prisms, containing 5 mols. H_2O ; the *calcium* compound, $\text{C}_{14}\text{H}_{10}\text{CaO}_{10} + 4\text{H}_2\text{O}$, is little soluble in cold, readily in hot water, and forms hard nodules; the *basic lead salt* is a white flocculent precipitate; the *potassium* and *sodium* salts form thin yellowish needles, readily soluble in water.

With ammonium carbonate gallic acid yields *gallo-carboxylic acid*, identical with that obtained from pyrogallol. O. H.

Orthoethylphenol. By W. SUIDA and S. PLOHN (*Wien. Akad. Ber.* [2 Abth.], **81**, 245—253).—The authors instituted the research in order to determine whether one of the isomeric ethylphenols is produced by the action of nitrous acid on amidoethylbenzene. They employed a mixture of the two amidoethylbenzenes, which on treatment with nitrous acid yielded a heavy oil; this was separated into two portions: one boiling between 206—208° C., the other between 212—215° C.

The former is ethylphenol. It is a slightly yellowish liquid which is highly refractive. It boils at 210·78° (corr.), and remains liquid at -18°. It is easily soluble in alcohol and ether, but only very slightly so in water. It combines with the alkalis and with barium, calcium, silver, and lead. *The barium salt*, $(C_6H_4Et.O)_2Ba$, crystallises in white plates which decompose at 100°.

Mononitroethylphenol.—The oil boiling between 212—215° readily forms a barium salt which crystallises in orange-yellow plates of the composition $[C_6H_3Et(NO_2).O]_2Ba + H_2O$. This salt is much more stable than that of ethylphenol.

Ethylphenolsulphonic acid.—The barium salt, $(C_6H_5SO_4)_2Ba$, is obtained by dissolving ethylphenol in sulphuric acid and neutralising the diluted solution with barium carbonate. The salt crystallises in colourless nearly plates which contain water of crystallisation.

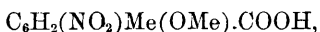
Bromine Derivative of Ethylphenol.—This compound is formed by cautiously adding bromine to ethylphenol and allowing the mixture to stand for a day; hydrobromic acid is freely evolved, and the product is then washed with soda solution and dried over calcium chloride. On fractionating, more hydrobromic acid is given off, and at the same time the characteristic odour of styrol is evolved, a styrol compound being formed in the same manner that styrol is formed by distilling phenylbromethyl. The liquid which distils over at 265—266° has a bright yellow colour. *The barium salt*, $(C_6H_3BrEt.O)_2Ba + 12H_2O$, is obtained by evaporating the liquid with baryta-water. It crystallises from alcohol in colourless plates. On decomposing the barium salt, bromoxystyrol is obtained as an oily liquid boiling constantly at 265°. It is very slightly soluble in water, but easily so in alcohol and ether.

Nitro-derivative.—This compound is formed when ethylphenol is allowed to drop slowly into cooled fuming nitric acid. It separates out as a heavy bright yellow oil when the crude product of the reaction is agitated with water. *The lead salt* is obtained by neutralising the above liquid with ammonia and adding lead acetate. It has an orange-yellow colour, and is explosive. *The barium salt* crystallises from alcohol in bright yellow plates. The analyses of the salt show that the body is a dinitroethylphenol. Ethylphenol is not oxidised by dilute nitric acid, manganese dioxide and sulphuric acid, or potassium dichromate and sulphuric acid. By fusing it with potash, however, salicylic acid is formed.

J. I. W.

Oxidation of the Methyl Ether of Paraxylenol. By F. CANZONERI (*Gazzetta*, **10**, 516—517).—For the sake of comparison with the results obtained by the oxidation of the methyl and ethyl ethers

of thymol (this Journal, 1880, Abstr., 246), it seemed desirable to study the behaviour of the methyl ether of paraxylonol under similar circumstances. The ether prepared in the usual manner boils at 194° , and is easily oxidised by nitric acid at first, but it requires two days' boiling to complete the action. The crystalline product which is deposited on standing is a mixture of acids, from which the author succeeded in separating one, the less soluble, crystallising in slender needles (m. p. 172° and 174°); and another in small, ill-defined crystals (m. p. 156 — 160°). An analysis of the first gave numbers agreeing with those required by methoxynitrotoluic acid,



and from its melting point it would seem to be identical with that previously obtained by the authors (*loc. cit.*), Me : OMe : COOH = [1 : 3 : 4]; the other is probably the methoxytoluic acid of Gerichten and Rossler (this Journal, 1879, Abstr., 323), Me : OMe : COOH = [1 : 2 : 4]. The amount of substance, however, was insufficient to definitely establish this.

C. E. G.

Dimethylresorcinol. By O. DE CONINCK (*Bull. Soc. Chim.* [2], **34**, 149—150).—A better means of preparing dimethylresorcinol than that generally used, is to dissolve 1 part resorcinol in methyl alcohol, then add 1.5 part fused potash, and 3 parts methyl iodide, and heat the mixture at 250° for five or six hours. The product is poured into water, when a layer consisting of monomethyl- and dimethylresorcinol and unaltered resorcinol separates. This and the aqueous solutions are separately extracted with ether, the extracts mixed and distilled in a current of steam. The distillate is shaken with ether, and the ether expelled from the solution. The residue, an oily liquid (b. p. 215°), consisting of impure dimethylresorcinol, may be purified by repeated fractional distillation, or better, by shaking the fraction (b. p. 205 — 220°) with separate quantities of potash-ley diluted with half its volume of water until, on adding a fresh quantity of alkali, no rise in temperature takes place. The dimethylresorcinol (b. p. 210 — 212°) thus obtained is an oily refractive liquid, colourless, or of a faint yellow, having an ethereal odour and sp. gr. 1.075.

L. T. O'S.

Dipropylresorcinol and some its Derivatives. By K. KARIOF (*Ber.*, **13**, 1677—1679).—Dipropylresorcinol, $\text{C}_6\text{H}_4(\text{OPr})_2$, is prepared in a similar manner to the methyl ether, viz., by heating 1 mol. resorcinol, 2 mols. potassium propyl sulphate, and 2 mols. potash together in sealed tubes at 160° . It is a colourless liquid, heavier than water, and of feeble odour. It is sparingly soluble in cold water, more so in hot, and mixes easily with the other ordinary solvents. It boils at 251° and is volatile in steam. The vapour-density was found to be 7.016. Ferric chloride yields no coloration with its aqueous solution.

Tetrachlorodipropylresorcinol is obtained by passing chlorine into the above compound diluted with glacial acetic acid. It is a slightly coloured liquid, heavier than water. It decomposes at 100° .

Monobromodipropylresorcinol is obtained by the action of bromine

on dipropylresorcinol dissolved in glacial acetic acid. It crystallises in slender, colourless, silky needles; it is soluble in alcohol, but only sparingly in water. It melts at 70—71°, and may be sublimed.

P. P. B.

Resorcinol Derivatives. By F. TIEMANN and A. PARRISIUS (*Ber.*, **13**, 2354—2381).—*β-Resorcylic acid*, $C_6H_3(OH)(OH).COOH$ [1:3:4], can be obtained by fusing umbelliferone or *β-resorcyraldehyde* with potash at a temperature between 160° and 190° for six minutes. The fused mass is dissolved in water, acidified with sulphuric acid, and extracted with ether. The ethereal extract having been shaken up with a concentrated solution of acid sodium sulphite, in order to remove traces of the aldehyde, is allowed to evaporate, when crystals of the pure acid are deposited.

The acids obtained by Blomstrand (*Ber.*, **5**, 1088; this Journal, 1873, 505) from toluenedisulphonic acid; by Ascher (*Annalen*, **161**, 7) from paranitrotoluenesulphonic acid, and by Senhofer and Brunner (*Wien. Akad. Ber.*, 1879, **2**, 504) by the action of ammonium carbonate on resorcinol are all identical with *β-resorcylic acid* from umbelliferone or *β-resorcyraldehyde*.

A mixture of mono- and di-methylresorcinol is formed by treating a solution of sodium resorcinol in methyl alcohol with methyl iodide. The crude product is diluted with water and evaporated to expel methyl alcohol; the residue is acidified with hydrochloric acid and saturated with common salt, when an oily liquid is formed which is dissolved out in ether. When the extract is shaken up with a 10 per cent. solution of soda, the monomethyl derivative dissolves in the alkaline liquid and the dimethyl ether remains in the ether.

Monomethylresorcinol, $C_6H_4(OMe).OH$ [1:3], is a colourless, oily liquid (b. p. 243°), soluble in hot water, alcohol, ether, and benzene. The pure compound is slightly volatile in a current of steam, but considerable quantities are carried over if it is mixed with dimethylresorcinol.

Tribromomethylresorcinol, $C_6HBr_3(OMe).OH$, formed by adding bromine to an ethereal solution of monomethylresorcinol, crystallises in colourless needles (m. p. 104°), soluble in ether, alcohol, benzene, and light petroleum.

Potassium methylresorcinolsulphate, $C_6H_4(OMe).OSO_3K$, is formed when potassium pyrosulphate is added to a solution of methylresorcinol in potash. The salt crystallises in white plates, soluble in hot alcohol and water. It is decomposed by acids.

Dimethylresorcinol, $C_6H_4(OMe)(OMe)$ [1:3], is a mobile liquid (b. p. 214°), freely soluble in alcohol, ether, and benzene. With bromine it yields *dibromodimethylresorcinol*, $C_6H_2Br_2(OMe)_2$, a crystalline powder (m. p. 141°), soluble in alcohol, ether, and benzene.

A mixture of four aldehyde derivatives is produced by adding gradually 16 parts of chloroform to a boiling solution of monomethylresorcinol (1) and soda (16) in 100 parts of water. After boiling for five hours the liquid is acidified with sulphuric acid and extracted with ether. The extract is shaken up with a solution of acid sodium sulphite. This compound is decomposed by sulphuric acid and the product treated with ether. The crystalline mass which remains,

after the evaporation of the ether, is dissolved in water and distilled in a current of steam, when orthomethoxypara-hydroxybenzaldehyde, $C_6H_3(COH)(OMe).OH$ [1 : 2 : 4], is left in the retort. The distillate is shaken up with ether and the solution mixed with light petroleum; on evaporating the ethereal extract, α -methylresorcinodialdehyde, $C_6H_2(COH)_2(OMe).OH$, remains.

The light petroleum has extracted from the ethereal solution *paramethoxysalicylaldehyde*, $C_6H_3(COH)(OH).OMe$ [1 : 2 : 4], and β -methylresorcinodialdehyde, $C_6H_2(COH)_2(OH).OMe$, which may be separated by the insolubility of the former compound in hot water.

Orthomethoxyparabenzaldehyde crystallises in lustrous plates (m. p. 153°), soluble in alcohol, ether, and chloroform, and also in boiling water, benzene, and light petroleum. The aqueous solution gives a faint violet coloration with ferric chloride, and a white crystalline precipitate with silver nitrate or lead acetate in presence of ammonia. The acetic derivative, $C_6H_3(COH)(OMe).O\bar{A}c$, formed by the action of an ethereal solution of acetic anhydride on the potassium salt of the aldehyde, crystallises in needles (m. p. 86°) which dissolve in alcohol, ether, benzene, and chloroform. The compound $C_6H_3(OMe)(O\bar{A}c).CH(O\bar{A}c)_2$ [1 : 2 : 4] is produced when the aldehyde is digested with acetic anhydride.

Orthomethoxyparoxybenzoic acid, $C_6H_3(COOH)(OMe).OH$ [1 : 2 : 4], is obtained by the oxidation of acetorthomethoxyparoxybenzaldehyde (in a finely-divided state) by potassium permanganate as a syrupy liquid which slowly crystallises.

Dimethyl β -resorcyaldehyde, $C_6H_3(COH)(OMe)(OMe)$ [1 : 2 : 4], can be prepared by the action of methyl iodide on orthomethoxyparabenzaldehyde or β -resorcyaldehyde. It crystallises in needles (m. p. 68°), soluble in alcohol, ether, benzene, and light petroleum, and is volatile in a current of steam.

Paramethoxysalicylaldehyde crystallises in glistening white plates (m. p. 62°), having a pleasant aromatic odour. The crystals are soluble in alcohol, ether, benzene, and light petroleum. It resembles salicylaldehyde in its reactions with ammonia, soda, and ferric chloride.

Methyl paramethoxysalicylate, $C_6H_3(COOMe)(OH).OMe$ [1 : 2 : 4], prepared by the action of methyl iodide on a solution of disodium β -resorcyate, on saponification yields the free acid in glistening needles (m. p. 154°), which dissolve in alcohol, ether, and hot water.

The acid produces an intense reddish-violet coloration with ferric chloride. Neutral solutions give sparingly soluble precipitates with lead and silver salts, and alkaline solutions yield a sparingly soluble crystalline precipitate with barium chloride.

α -Monomethylresorcinodialdehyde forms white needle-shaped crystals (m. p. 179°), soluble in ether, alcohol, chloroform, benzene, glacial acetic acid, and hot water. In presence of ammonia the aqueous solution gives with lead acetate a yellow precipitate, with copper sulphate a prismatic precipitate, and reduces silver nitrate.

The β -compound also forms needle-shaped crystals (m. p. 88°), soluble in alcohol, ether, benzene, light petroleum, and hot water. The solution mixed with a few drops of ammonia gives with lead

acetate a yellow, with copper sulphate a green, and with silver nitrate a white precipitate.

Barth (*Annalen*, **159**, 217; **164**, 109; *Wien. Akad. Ber.*, 1872 [2], 89; 1874 [2], 89) has shown that α -resorcylic acid from disulphobenzoic acid has the constitution $C_6H_3(COOH)(OH)(OH)$ [1 : 3 : 5], and since the β -acid is [1 : 2 : 4] the third isomeride, prepared by Senhofer and Brunner, will be represented by $COOH : OH : OH$ [1 : 2 : 6].

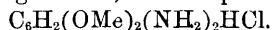
W. C. W.

Derivatives of Dimethylquinol. By K. KARIOF (*Ber.*, **13**, 1673—1677).—Dimethylquinol-disulphonic acid is obtained by heating dimethylquinol with concentrated sulphuric acid at 120—125°. The solution so prepared is treated with water, and the barium salt prepared by neutralising with barium carbonate.

Barium dimethylquinol-disulphonate, $C_6H_2(OMe)_2(SO_3)_2Ba$, is an amorphous white substance easily soluble in water, but insoluble in alcohol. The *potassium* salt is prepared by acting on the barium salt with potassium sulphate; it forms large, colourless, tabular crystals, which dissolve in water, but are insoluble in alcohol. The *ammonium* salt crystallises in large colourless prisms, soluble in water, but insoluble in alcohol. The *zinc* salt crystallises in silky needles, soluble in water, but insoluble in alcohol. The *silver* salt is easily soluble in water, and blackens on exposure to light. The *lead* salt is a colourless amorphous powder, which is sparingly soluble in water.

Dimethylquinol-disulphonic acid is obtained by decomposing the barium salt with sulphuric acid; it crystallises from water in colourless needles, soluble in water and alcohol, but insoluble in ether. Ferric chloride gives a bluish-violet coloration with the solution of its soluble salts.

By the reduction of dinitro-dimethylquinol with tin and hydrochloric acid at 40°, a hydrochloride of *dianido-dimethylquinol* has been obtained; it crystallises in long, colourless, silky needles (m. p. 169°), its composition, after drying at 100°, is in all probability—



P. P. B.

Isomerides of Phloroglucol. By A. GAUTIER (*Bull. Soc. Chim.* [2], **33**, 583—587).—The author, by fusing certain substances with potash in a manner similar to that employed in preparing phloroglucol from phlorizin, has obtained isomerides of that compound, which he proposes to distinguish by the generic name of glucins.

Enoglucol, prepared from the red colouring matter of wine, crystallises with $2H_2O$, which it loses at 100°. It closely resembles phloroglucol in most of its properties, but differs from it in its melting point (208.5°) and in giving no coloration, or only of the feeblest, with ferric chloride.

Querciglucol ($3C_6H_6O_3 \cdot 2H_2O$), from quercetin, is sparingly soluble in water; the dry substance melts at 174°. It gives no coloration with ferric salts.

Phenoglucol.—On fusing phenol with soda, a small quantity of a substance of the formula $C_6H_6O_3 \cdot 2H_2O$ is obtained in large rhomboidal prisms (m. p. 200.5°), giving a feeble violet coloration with ferric chloride. At the time these experiments were made the author

was not aware that Barth and Schroeder had obtained phloroglucol by the action of fused soda on phenol, but he does not consider the identity of the products from phenol and from phlorizin as definitely settled. CEnoglucol and querciglucol he believes to be isomerides of phloroglucol. C. E. G.

Combination of Titanium Tetrachloride and Benzoic Chloride. By A. BERTRAND (*Bull. Soc. Chim.* [2], **34**, 631).—Titanium tetrachloride and benzoic chloride combine directly, with development of heat, to form a double chloride having the composition



It forms beautiful yellow crystals (m. p. 65°), and the crystallisation is accompanied by a development of heat and a peculiar noise. It attacks the eyes like benzoic chloride, and with water and alkalis behaves like a mixture of the two chlorides. Titanium chloride appears to combine with the majority of the acid chlorides, and analogous compounds are formed by stannic chloride.

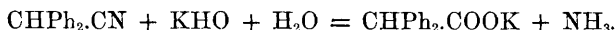
When titanium chloride is purified from chlorine by distillation over mercury, the distillate contains small quantities of that metal, possibly in the form of a double chloride of mercury and titanium. A better method is to distil the chloride two or three times with a small quantity of reduced iron; the distillate contains neither iron nor dilitanium hexachloride. C. H. B.

Synthesis of Benzoyl-propionic Acid. By E. BURCKER (*Bull. Soc. Chim.* [2], **35**, 17).—In presence of aluminium chloride, benzene and succinic anhydride react slowly in the cold, violently if heated, forming benzoyl-propionic acid, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_2\text{H}_4 \cdot \text{COOH}$. This acid forms nacreous crystals which are insoluble in cold water, but dissolve in hot water, alcohol, ether, and benzene. They melt at 116° , and at a higher temperature are converted into a red product which crystallises on cooling. *Barium benzene-propionate* ($\text{C}_{10}\text{H}_9\text{O}_3$)₂Ba, crystallises in colourless needles, usually in mamillary groups. *Ferric benzene-propionate* is obtained as a voluminous flesh-coloured precipitate by adding ferric chloride to an alkaline solution of the acid. C. H. B.

Synthesis of Diphenylacetic Acid. By C. FRIEDEL and M. BALSOHN (*Bull. Soc. Chim.* [2], **33**, 589—591).—Monobromodiphenylmethane is heated at 165° for 18 hours with two-thirds of its weight of mercuric cyanide, the product exhausted with benzene, and the benzene solution distilled to dryness. The residue is then boiled with alcoholic potash until ammonia is no longer evolved, and the solution poured into water and agitated with ether. The clear aqueous solution, after the dissolved ether has been removed by heating, is acidified with hydrochloric acid, when the diphenylacetic acid is precipitated, and may be purified by crystallisation from boiling water.

In this process, the mercuric cyanide first converts the monobromodiphenylmethane into the corresponding cyanide, CHPh_2CN ,

which is then decomposed by boiling with potash, yielding diphenyl-acetic acid—



C. E. G.

Dinitrohydrocinnamic Acid and its Derivatives. By S. GABRIEL and J. ZIMMERMANN (*Ber.*, **13**, 1680—1684).—*Orthonitrohydrocinnamic acid*, $\text{C}_6\text{H}_4(\text{NO}_2).\text{C}_2\text{H}_4.\text{COOH}$, is obtained by converting the hydrochloride of the nitroamido-derivative (m. p. 138°), described by the authors (this Journal, **36**, 640), into the diazo-compound, and boiling this with absolute alcohol. In this way orthonitrohydrocinnamic acid and its ethyl salt are obtained, from which the former is separated by dissolving it in ammonia and precipitating it from its ammonia salt.

Orthonitrohydrocinnamic acid crystallises in small yellow prisms (m. p. 113°). When reduced with tin and hydrochloric acid, it yields *hydrocarbostyryl*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH} \\ \text{C}_2\text{H}_4 \end{smallmatrix} > \text{CO}$; this crystallises from water in beautiful lustrous needles (m. p. 169°).

Parabromorthonitrohydrocinnamic acid, $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2).\text{C}_2\text{H}_4.\text{COOH}$ [1 : 3 : 4], is obtained by acting on the chloride of the above-mentioned diazonitrohydrocinnamic acid with hydrobromic acid; it crystallises from dilute alcohol in yellow feathery flat crystals (m. p. 141 — 142.5°). The same acid is obtained together with an isomeride by the nitration of parabromhydrocinnamic acid; it is separated from its isomeride by the sparing solubility of its barium salt. This acid on reduction yields *parabromhydrocarbostyryl*, $\text{C}_6\text{H}_3\text{Br} < \begin{smallmatrix} \text{C}_2\text{H}_4 \\ \text{NH} \end{smallmatrix} > \text{CO}$, which crystallises from dilute alcohol in long, flat, shining needles, easily soluble in the ordinary solvents (m. p. 178°).

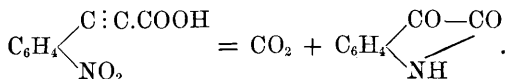
Parabromometanitrohydrocinnamic acid, $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2).\text{C}_2\text{H}_4.\text{COOH}$ [1 : 2 : 4], forms a more soluble barium salt than the above, and is easily separated from it by this means, it has not been obtained quite free from its isomeride. On reduction, it yields a metamidoparabromo-derivative, the hydrochloride of which crystallises in long silky needles. The free acid crystallises from hot water in long prisms (m. p. 117 — 119°), soluble in ordinary solvents. P. P. B.

Relation of Cinnamic Acid to the Indigo Group. By A. BAEYER (*Ber.*, **13**, 2254—2263).—After giving a short historical sketch of the different steps which led to the discovery of the artificial formation of indigo, the author describes the preparation of indigo-blue from cinnamic acid. *Orthonitrocinnamic acid*, $\text{C}_9\text{H}_7\text{NO}_4$ (m. p. 240°) is best prepared by the process described by Beilstein and Kuhlberg (*Ann.*, **163**, 125), which converts about 60 per cent. of the cinnamic acid into the orthonitro-acid. The ortho- and para-acids are separated by means of the difference of their solubility in ether. Ethyl orthonitrocinnamate forms rhombic crystals ($a : b : c = 0.9265 : 1 : 0.5174$) which melt at 44° . This ortho-acid can easily be identified by the blue colour which is produced when it is dissolved in warm sulphuric acid. *Dibromonitrocinnamic acid*, formed by the direct addition of

bromine to the nitro-acid, crystallises in colourless needles or plates which melt at 180° with decomposition. The crystals are soluble in hot water and in benzene. The ethyl and methyl salts of this acid melt respectively at 110° and 98° . When a solution of the dibromo-acid in caustic alkalis is gently warmed, it changes into orthonitropropionic acid and isatin. Indigo-blue is also formed if the solution is boiled, and if zinc-dust is added to the mixture, indole is produced.

If a solution of dibromorthonitrocinnamic acid in excess of caustic alkali is allowed to stand for some time, and an acid is then added, a white precipitate of *orthonitrophenylpropionic acid* is thrown down. The acid may be obtained in colourless needles by careful recrystallisation from hot water; it melts at 155° with decomposition. The potassium and sodium salts of this acid are freely soluble in water, but much less soluble in the presence of free alkali. The *silver* salt explodes when heated. The *ethyl* salt is deposited from an ethereal solution in large tables (m. p. 60°).

Orthonitroacetylene, $C_6H_5NO_2$, is prepared by the action of water at 150° on nitrophenylpropionic acid or by boiling an aqueous solution of the acid in a flask provided with an upright condenser. The product is distilled in a current of steam, and the nitroacetylene purified by recrystallisation from alcohol. It forms colourless needles (m. p. 81°) which acquire a yellow colour on exposure to light. The crystals dissolve freely in hot water and in most solvents. An ammoniacal solution of silver nitrate yields a yellowish-white, and ammoniacal cuprous chloride solution forms a red precipitate with nitroacetylene. On reduction with zinc-dust and ammonia, an oily base is produced which has the peculiar odour characteristic of the indigo vat. The decomposition of orthonitropropionic acid by the action of a hot solution of potash may be advantageously employed as a method for preparing isatin, 86 per cent. of the theoretical yield being obtained.



On the addition of a small quantity of grape-sugar to a hot solution of the propionic acid in dilute potash, needle-shaped crystals of pure indigo-blue free from indirubin are deposited. This method yields a better result than is obtained by the direct production of indigo from orthonitrodibromocinnamic acid.

Orthonitrophenylchlorolactic acid, $C_6H_5ClNO_2$, is formed together with orthonitrochlorostyrol, when chlorine is passed into a solution of orthonitrocinnamic acid in dilute soda solution. The bye-product is removed by filtration, and the filtrate acidified and extracted with ether.

The residue obtained by evaporating the ethereal extract is dissolved in benzene, and the solution mixed with light petroleum, when the chlorolactic acid is precipitated as a white crystalline mass (m. p. 119°). This acid is converted into indole by reduction with sodium amalgam or with ferrous sulphate in an alkaline solution.

By the action of alcoholic potash, it is converted into *orthonitrophenylloxycrylic acid*, $C_6H_7NO_5$. When slowly heated, orthonitro-

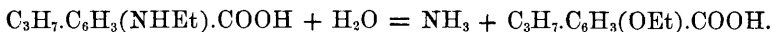
phenyloxyacrylic acid begins to melt at 110° , with decomposition, carbonic oxide and indigo-blue being formed. This acid is also split up by continued boiling with water or dilute sulphuric acid.

W. C. W.

Hydroxycumic Acid. By E. v. LIPMANN and R. LANGE (*Ber.*, **13**, 1660—1664).—When nitrocumic acid (m. p. 158°) is reduced by ammonium sulphide, it is converted into amidocumic acid, which after purification by crystallisation from water, melts at 129° . The acid (m. p. 104°) which Paternò and Fileti (*Ber.*, **12**, 81) believed to be an isomeride, melts at 129° after crystallisation from water. The hydrochloride of amidocumic acid gives a brownish-violet precipitate with ferric chloride.

Silver amidocumate, $C_3H_7.C_6H_3(NH_2).COOAg$, is obtained as a white flocculent precipitate. *Zinc amidocumate* $(C_{10}H_{12}NO_2)_2Zn + 3H_2O$, crystallises from hot water in brownish needles.

By heating amidocumic acid with ethyl iodide at 108° , the ethiodide of amidocumic acid is obtained which is decomposed by alkalis, yielding ethoxycumic acid, thus:



Ethoxycumic acid is a crystalline powder (m. p. 140°), sparingly soluble in water. The *silver* salt, $C_3H_7.C_6H_3(OEt).COOAg$, is a red precipitate, blackening on exposure to the air. The *cadmium* salt, $[C_3H_7.C_6H_3(OEt).COO]_2Cd$, crystallises in red needles.

Hydroxycumic acid, $C_3H_7.C_6H_3(HO).COOH$, is obtained by passing nitric oxide into solution of the hydrochloride or nitrate of amidocumic acid. It crystallises in colourless prisms (m. p. $138-140^{\circ}$). Its lead salt is pale yellow, whilst the silver salt is colourless. A comparison of this acid with thymol hydroxycumic acid (Barth, this Journal, **36**, 158), shows them to be identical, and hence its constitution is $COOH : OH : C_3H_7$ [1 : 3 : 4].

P. P. B.

Phenoxycinnamic Acid. By A. OGLIALORO (*Gazzetta*, **10**, 481—485).—This acid is formed by the action of benzaldehyde and acetic anhydride on crude sodium phenylglycollate, obtained by neutralising crude phenylglycollic acid (prepared by Giacosa's method) with sodium carbonate. After the mixture has been heated at about 150° for eight hours, the liquid product is digested with water to remove acetic anhydride, and the pasty residue treated with sodium carbonate solution, which dissolves the acids and leaves the unaltered benzaldehyde. On adding an acid to the alkaline solution, a mixture of phenoxycinnamic and cinnamic acids is precipitated; the formation of the latter is probably due to the presence of excess of soda in the phenolglycollate, which, reacting with the acetic anhydride and benzaldehyde yields cinnamic acid. The two acids are easily separated by boiling the product repeatedly with water, which leaves the phenoxycinnamic acid undissolved; it may be purified by recrystallisation from dilute alcohol with aid of animal charcoal. The pure acid forms colourless lustrous prisms of the formula, $C_{15}H_{12}O_3$, and is formed in the following manner: $Ph.CO.H + CH_2(OPh).COOH = CHPh : C(OPh).COOH$

+ H₂O. It is very sparingly soluble in water, but easily in alcohol, from which it crystallises by spontaneous evaporation in large well-defined transparent prisms (m. p. 179—180°). Its silver salt is thrown down as a white crystalline powder, on adding silver nitrate to a solution of the ammonium salt: it is sparingly soluble in boiling water. When the acid is boiled with baryta-water, a large portion resinifies, but if the solution prepared in the cold be evaporated at the ordinary temperature over lime or sulphuric acid, the barium salt may be obtained in large transparent crystals. The author intends to continue this research with other aldehydes, and states that he is studying the action of benzaldehyde on hydrocinnamic acid in presence of acetic anhydride. C. E. G.

Synthesis of Tropic Acid from Acetophenone. By A. SPIEGEL *Ber.*, **14**, 235—240).—If strong hydrochloric acid (1 mol.) is allowed to drop slowly into a well-cooled vessel containing the equivalent quantities of acetophenone and pure potassium cyanide moistened with water, *acetophenone cyanhydrin*, CH₃.CPh(OH).CN, is obtained as an oily liquid. By the action of twice its volume of strong hydrochloric acid at 130°, it is converted into *chlorohydratropic acid* (m. p. 89°), CH₃.CClPh.COOH, which Ladenburg (*Ber.*, **12**, 947, this Journal, 1879, Abstr., 720) obtained by the action of phosphorus pentachloride on tropic acid. This acid is most easily purified by precipitating the chloroform solution with light petroleum. It is converted into atropic acid by boiling with soda, and by the action of sodium carbonate solution at 120° for several hours it is converted into tropic acid, which is identical with the tropic acid from atropine. From this synthesis it appears that the constitution of tropic acid is correctly represented by Fittig's formula, CH₃.CPh(OH).COOH.

By the action of nascent hydrocyanic acid on benzaldehyde, the nitril of mandelic acid is formed; this may be converted by treatment with hydrochloric acid at 130° into phenylchloroacetic acid, from which mandelic and phenylacetic acids can be prepared.

Phenylglyoxylic acid also combines with nascent hydrocyanic acid. W. C. W.

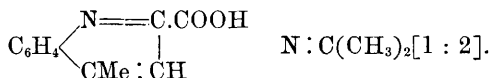
On Quercitannic Acid. By C. ETTL (*Wien. Akad. Ber.* [2 Abth.], **81**, 495—511).—In order to extract the acids from oak-bark, the author dries and then powders it, and afterwards passes it over a sieve, whereby the greater part of the red bark is separated from the bast fibres. The former is boiled with alcohol and filtered; the filtrate is shaken with a mixture of ether and ethyl acetate until it no longer dissolves tannic acid; and the ether is then distilled off. The residue, which contains alcohol, deposits crystals of ellagic acid: these are filtered off, and the tannic acid obtained by evaporating the filtrate. *Quercitannic acid* obtained by the above method is a reddish-white powder. Its alcoholic solution is coloured dark blue by ferric chloride. On analysis, it yields numbers which agree with either of the formulæ, C₁₇H₁₆O₉ or C₁₉H₁₈O₁₀.

When heated at 130—140°, it loses water, and its anhydride is formed, and as this forms a barium compound of the composition

$C_{34}H_{28}BaO_{17}$, the formula of the tannic acid will be $C_{17}H_{16}O_9$. The anhydride exists in the bark, and is prepared therefrom by evaporating the alcoholic extract on a water-bath to a small volume, and then diluting it with water containing a trace of hydrochloric acid. As the mixture cools, a red precipitate is formed, which on recrystallisation yields the pure anhydride: it is also formed when the tannic acid is heated with dilute acids or alkalis. By the action of acids in sealed tubes, neither phenol nor any other acid except gallic acid is formed. By heating with hydrochloric acid, however, a large volume of gas which burns with a greenish flame is generated. The author considers it probable that the tannic acid of oak-bark consists of two molecules of gallic acid united by the loss of one molecule of water, $2(C_7H_6O_5)H_2O = C_{14}H_{10}O_9$. He affirms that the acid is not a glucoside, and that the analysis and formula of the anhydride show that the body could not split up into a carbohydrate. J. I. W.

Sulphoterephthalic Acid. By P. SCHOOP (*Ber.*, **14**, 223—227).—Sulphoterephthalic acid is prepared by heating a mixture of strongly fuming sulphuric acid and terephthalic acid in sealed tubes at 250° . The contents of the tubes are poured into water; the unaltered terephthalic acid removed by filtration, and the filtrate neutralised with lead carbonate. By the decomposition of the lead salt with sulphuretted hydrogen, sulphoterephthalic acid is obtained as a hygroscopic strongly acid compound. It is dibasic, and its salts are freely soluble in water, but insoluble in most other solvents. The barium and calcium salts crystallise with $1\frac{1}{2}$ and the lead salt with 2 mols. H_2O . The amide, $C_8H_4O_4SO_3(NH_2)_2$, forms needle-shaped crystals, which melt above 300° . W. C. W.

Constitution of Aniluvitonic Acid. By C. BÖTTINGER (*Ber.*, **14**, 133—134).—Since the pyridinetricarboxylic acid, which is formed by the action of potassium permanganate on aniluvitonic acid, is identical with the acid obtained by the oxidation of uvitonic acid, it follows that aniluvitonic acid has the constitution:—



In γ -pyridinecarboxylic acid, the position of N and COOH is 1:4.

W. C. W.

Dimethyl α -Hydroxyuvitate. By C. BÖTTINGER (*Ber.*, **13**, 2345).—*Dimethyl α -oxyuvitate*, prepared by slowly adding strong sulphuric acid to a solution of α -oxyuvitic acid in methyl alcohol, and heating the mixture at 50° , is deposited from a hot alcoholic solution in glistening plates (m. p. 129°). This substance appears to be identical with Jacobsen's (*Ber.*, **13**, 2050) dimethyl salt of ortho-para-oxyuvitic acid. W. C. W.

Preparation of Skatole from Indigo. By A. BAEYER (*Ber.*, **13**, 2339—2340).—A mixture of skatole and indole is obtained by boiling finely-ground indigo with tin and hydrochloric acid until the

mixture assumes a yellow colour. The precipitate is washed with water, and, while moist, is mixed with an excess of zinc-dust, and distilled in a metallic retort. The oily distillate is freed from aniline by treatment with hydrochloric acid, and is then extracted with light petroleum. The precipitate, which is thrown down when a solution of picric acid in benzene is added to this extract, yields, on distillation with ammonia, a mixture of skatole and indole. If moderately concentrated potash solution is substituted for the ammonia, the indole is decomposed, and skatole alone is obtained. The skatole prepared from indigo has a penetrating odour, but is devoid of the nauseous smell characteristic of the skatole obtained from albumin. W. C. W.

Action of Ammonia on Monobromodiphenylmethane. By C. FRIEDEL and M. BALSOHN (*Bull. Soc. Chim.* [2], **33**, 587—589).—Alcoholic ammonia acts readily on monobromodiphenylmethane, CPh_2HBr , giving ammonium bromide and ethyl benzhydrylic ether. With aqueous ammonia, however, the action is different; at first the mass becomes liquid, but on standing 48 hours, it again becomes solid. Boiled with alcohol, it dissolves, and, on cooling, the secondary amine of diphenylmethane $(\text{CHPh}_2)_2\text{HN}$, is deposited in slender needles (m. p. 136°). The author proposes to call this compound *dibenzhydrylamine*, regarding the radical of benzhydrol as “benzhydryl.” The base is soluble in benzene and in hot alcohol, but only sparingly so when cold, and is insoluble in water. It is indifferent towards acids, and is not acted on by ethyl chloride or acetic chloride. It forms a crystalline compound with picric acid.

Benzhydrylamine, NH_2CHPh_2 .—The alcoholic mother-liquors, when concentrated, deposit a further quantity of the secondary amine, mixed with the hydrobromide of benzhydrylamine, which may be dissolved out by treating the mass with boiling water. On adding ammonia to the solution, the free base is precipitated as an oil, which solidifies after a time. It boils at 295° , and unites readily with acids, yielding crystalline salts, sparingly soluble in cold water, but readily in hot water. The *platinochloride* crystallises in orange-coloured plates. A small quantity of benzhydrol is also formed by the action of the water on the monobromodiphenylmethane. C. E. G.

Action of Sulphuric Acid on Phenyl-acetylene. By C. FRIEDEL and M. BALSOHN (*Bull. Soc. Chim.* [2], **35**, 54—56).—The phenyl-acetylene employed was obtained by the action of alcoholic potash on styrolene bromide prepared by the action of bromine on perfectly pure ethyl-benzene. A violent reaction takes place when it is mixed with concentrated sulphuric acid, accompanied by development of heat, evolution of sulphurous anhydride, and production of a carbonaceous mass. When, however, the acid is diluted with one-half or one-third its volume of water, the phenyl-acetylene gradually dissolves on agitation, the liquid becoming hot, and acquiring a brown colour. On adding water and distilling the oily liquid which separates, methyl phenyl ketone, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$, is obtained. It boils at about 200° , melts at $16\text{--}17^\circ$, and remains superfused even at -5 to -6° , but immediately crystallises on adding a fragment of the solid substance. The

action of sulphuric acid on phenyl-acetylene causes it to take up a molecule of water, with formation of a ketone, and not of an alcohol. No alcohol is yet known in which the hydroxyl group is united directly with a non-saturated group. If such compounds exist, they must be very unstable, and readily convertible into the isomeric ketones or aldehydes.

C. H. B.

Ethyl-naphthalene. By G. CARNELUTTI (*Ber.*, **13**, 1671—1673).—The author has prepared this hydrocarbon according to the method of Fittig and Remsen (*Annalen*, **79**, 118). It is a colourless, strongly refractive liquid, distilling at 100° under 2—3 mm. pressure, and under 757·7 mm. pressure the greater portion distils at 257—259·5°, a portion, however, being decomposed. Its vapour-density was found to be 77·27 ($H=1$); its sp. gr. 1·0204 at 0°, and 1·0123 at 119°.

The *picrate* of *ethyl-naphthalene* crystallises from hot alcoholic solutions in fine lemon-yellow needles (m. p. 98°).

Bromine converts it into *tribromethyl-naphthalene*, which crystallises from ether in tufts of fine white needles.

P. P. B.

Acetyl- α -Naphthol. By G. TASSINARI (*Gazzetta*, **10**, 491).—The author has prepared acetyl- α -naphthol, and finds, contrary to the statement of Schaeffer (*Ber.*, **2**, 131), that it is crystalline. Schaeffer prepared his by the action of acetic chloride on the naphthol, whilst the author employed acetic anhydride and sodium acetate. It is not improbable that some impurity is present in the product obtained by the former process, and that this prevents it from crystallising. Acetyl- α -naphthol is very soluble in alcohol and in ether, from which it separates in large crystals (m. p. 49°).

C. E. G.

Action of Oxalic and Sulphuric Acids on Naphthol. By M. HÖNIG (*Wien. Akad. Ber.* [2], **81**, 479—485).—Grabowski (*Ber.*, **4**, 1871, 661—725) has shown that when a mixture of naphthol with oxalic and sulphuric acids is heated at 110—115° for some hours, a compound having the formula $C_{21}H_{12}O_2$ is formed, according to the equation $2C_{10}H_8O + CO_2 = C_{21}H_{12}O_2 + 2H_2O$.

Naphthol (2 parts) is heated with sulphuric acid (1 part) for some time on a water-bath, and then oxalic acid (1 part) is added, and the mixture heated at 135—140° for three to four hours. When cold, the contents of the flask are repeatedly boiled first with water, then with alcohol, and the residue is crystallised from chloroform several times. The formation of dicarbonyldinaphthylene (naphthanthraquinone) from naphthol is shown by the author by the equation $2C_{10}H_8O + 2CO = C_{22}H_{12}O_2 + 2H_2O$. It is not attacked by phosphorus pentachloride, acetic anhydride, or acetic chloride. It therefore contains no hydroxyl groups, and has probably the constitution $OC < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} > CO$. By fusing with potash, a body of the formula $C_{22}H_{14}O_3$ is obtained.

The *chlorine derivative*, $C_{22}H_{10}Cl_2O_2$, is formed when chlorine gas is passed through the chloroform solution of the body. On allowing the liquid to stand over lime, colourless crystals separate out.

The *bromine derivative*, $C_{22}H_{10}Br_2O_2$, is obtained by mixing the

chloroform solution with the theoretical amount of bromine dissolved in glacial acetic acid. It forms a flesh-coloured crystalline precipitate, which, on recrystallisation from chloroform, is obtained in monoclinic crystals. J. I. W.

α - and β -Dinaphthylene Oxide. By W. KNECHT and J. UNZEITIG (*Ber.*, **13**, 1724—1726).— α -Dinaphthylene oxide, $(C_{10}H_8)_2O$, is obtained in a manner similar to diphenylene oxide, by distilling α -naphthol with lead oxide. It crystallises in brownish-yellow needles, m. p. 180° , is insoluble in water, sparingly soluble in alcohol, and easily in benzene, carbon bisulphide, and ether. It is insoluble in cold concentrated sulphuric acid, but on warming it forms a grey solution, which becomes red on addition of nitric acid. Like diphenylene oxide it is not soluble in alkalis, nor is its oxygen removed by zinc-dust or hydriodic acid.

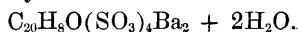
α -Dichlorodinaphthylene oxide, $C_{20}H_{10}Cl_2O$, is obtained by the action of phosphorus pentachloride on the oxide; it crystallises and sublimes in yellow needles, is easily soluble in benzene and glacial acetic acid, and sparingly soluble in alcohol, ether, and chloroform.

α -Dibromodinaphthylene oxide, $C_{20}H_{10}Br_2O$, is produced by the action of bromine on the oxide; it is a pale-yellow compound (m. p. 287°), sparingly soluble in benzene and glacial acetic acid.

α -Dinaphthylene oxide and picric acid form a compound, $C_{20}H_{12}O + 2C_6H_3(NO_2)_3OH$, crystallising in dark red needles (m. p. 167°). It is easily soluble in benzene, alcohol, and glacial acetic acid.

α -Dinitrodinaphthylene oxide, $C_{20}H_{10}(NO_2)_2O$, is produced with isomerides by acting with nitric acid at 100° on a solution of the oxide in glacial acetic acid; the chief product crystallises from benzene in yellow needles, m. p. 270° .

A sulphonic acid has been obtained; its barium salt is sparingly soluble in water, and crystallises in needles of the formula



The aqueous solution of the acid gives a blue fluorescence.

β -dinaphthylene oxide has been obtained from β -naphthol; it crystallises in yellow prisms (m. p. 155°). It is soluble in concentrated sulphuric acid, forming a red solution, which becomes dark blue on warming, and when diluted gives a red fluorescent solution. Its dichloro-derivative crystallises from benzene in yellow, silky, lustrous needles (m. p. 245°); with cold sulphuric acid it gives a red-brown coloration, becoming violet on warming. The dibromo-derivative crystallises in yellow needles (m. p. 247°). The dinitro-compound forms reddish orange needles (m. p. 221°).

The β -naphthylene oxide forms a tetrasulphonic acid, the barium salt of which crystallises in tablets, of the formula $C_{20}H_8O(SO_3)_4Ba_2 + 2H_2O$, and its aqueous solutions are fluorescent. The picric acid compound has a similar composition to that of the α -oxide, but is not as stable; it forms vermilion-coloured needles (m. p. 135°).

P. P. B.

Dinaphthylmethane. By M. RICHTER (*Ber.*, **13**, 1728—1729).—By the distillation of β -naphthoic acid the ketone was obtained, which

on reduction with phosphorus and hydriodic acid yields dinaphthylmethane ($C_{10}H_7$)₂CH₂; it melts at 92°, is soluble in alcohol and benzene, and crystallises in white needles. Its *dibromo*-derivative, $C_{21}H_{14}Br_2$, melts at 164°, and its *dinitro*-derivative at 150–160°. Its properties and those of its derivatives show it to be different from the dinaphthylmethane obtained by Grabowski (*Ber.*, **7**, 1605) from naphthalene and methal. P. P. B.

α - and β -Naphthylenephenylene Oxides. By v. J. ARX (*Ber.*, **13**, 1726–1728).— *α -Naphthylenephenylene oxide*, $C_{16}H_{10}O$, is obtained by heating phenol and α -naphthol with lead oxide; it crystallises from benzene in yellow needles (m. p. 178°); chloroform and ether dissolve it easily, but alcohol and glacial acetic acid only sparingly. It dissolves in hot concentrated sulphuric acid with a green colour, forming a tetra-sulphonic acid; its barium salt, $C_{16}H_8O(SO_3)_4Ba_2 + 4H_2O$, is easily soluble in water. The *picric acid* compound, $C_{16}H_{10}O + C_6H_2(NO_2)_3.OH$, is easily soluble in benzene, and crystallises in dark red needles (m. p. 165°); it is decomposed by alcohol.

Dichloronaphthalenephenylene oxide, $C_{16}H_8Cl_2O$, obtained by the action of phosphorus pentachloride on the oxide, or of chlorine on its solution in glacial acetic acid, is sparingly soluble in benzene, insoluble in alcohol and ether; it crystallises in slender white needles (m. p. 245°).

The *dibromo*-derivative, $C_{16}H_8Br_2O$, crystallises in yellowish-white needles (m. p. 284°), which are less soluble than the chloro-compound.

The *dinitro*-derivative, $C_{16}H_8(NO_2)_2O$, is easily soluble in ether, toluene, and glacial acetic acid, but only sparingly in alcohol; it has a yellow colour, and melts at 235°. *α -Naphthylenephenylene oxide* is oxidised by chromic acid, forming an acid, $C_{16}H_8O_3$, which is of a red colour, and melts at 140°; alcohol, glacial acetic acid, and benzene dissolve it easily, ether but sparingly. It dissolves in caustic alkalis and alkaline carbonates, forming red solutions. It is oxidised by potassium permanganate to phthalic acid. *α -Naphthylenephenylene oxide* is, therefore, isomeric with that obtained by Gräbe and Knecht (this Journal, **38**, 663) from phenylnaphthylcarbazon. The compound obtained by these authors is shown to be the *β -naphthylenephenylene oxide*, inasmuch as it is formed, although in small quantity, by distilling *β -naphthol* and phenol with lead oxide. P. P. B.

Decomposition of Rufigallic Acid. By J. SCHREDER (*Wien. Akad. Ber.* [2], **81**, 853–868).—By fusing rufigallic acid with potash, Malin (*Annalen*, **141**, 845) obtained a body, $C_6H_4O_3$, which he called oxyquinone. Kekulé (*Lehrb. Organ. Chem.*, **3**, 157) suggested that perhaps it stood in the same relation to pyrogallol as quinone does to quinol, and hence viewed it as a hydroxyl-derivative of quinone. Since then it has been shown that rufigallic acid is an anthracene-derivative, being hexoxyanthraquinone (Klobukowski, *Ber.*, **10**, 880). The author thinks the production of oxyquinone from this body rather improbable, and that a repetition of Malin's work is called for.

Having found the method proposed by Malin to be too violent, he modified the process as follows:—Rufigallic acid is added gradually to six times its weight of fused potash, the mixture froths up freely, and

as soon as this ceases the fusion is stopped; the product is dissolved in dilute sulphuric acid, filtered, and treated with ether in the usual way. The residue from the ethereal extract, which crystallises on standing, is treated with water, and filtered from the insoluble crystalline precipitate. Malin's oxyquinone may be purified by fractional precipitation of its alcoholic solution with lead acetate, &c. It crystallises in reddish-brown needles, easily soluble in alcohol, ether, and benzene, less so in hot water, and sparingly in cold water. It neither distils nor sublimes, and carbonises without melting. Its aqueous solution has a slightly acid reaction, and gives a bright blue coloration with ferric chloride (Malin obtained a violet coloration), which turns, in one or two minutes, to blue-green, and on addition of sodium carbonate bright red.

The analysis of the so-called oxyquinone corresponds with the formula $C_{24}H_{18}O_{11} + 4H_2O$; it loses its water on heating at 150° .

Distilled with 20 times its weight of zinc-dust in a current of hydrogen, it gave nearly the theoretical quantity of diphenyl. It is unaltered by long fusion with potash, or by boiling with zinc and sulphuric acid. Heating at 180° in a tube with hydriodic acid and phosphorus, it changes to a yellow amorphous substance, soluble only in hydriodic acid; with potassium hydrate and methyl iodide at the same temperature, it is converted into a brown resin.

The filtrate from the "oxyquinone" was found to contain salicylic acid and (1 : 3) oxybenzoic acid, some products of the decomposition of the hexoxydiphenyl ether, and two other acids, one of which, crystallising in needles, gave the reactions of the hydroxyisophthalic acid of Heine (this Journal, **38**, 549), and the other that of hydroxyterephthalic acid, from thymol, or α -hydroxyisophthalic acid, obtained by Heine (*loc. cit.*) by fusing γ -hydroxyisophthalic acid with potash.

It is probable that Malin's violet ferric chloride reaction was due to the presence of these acids.

The entire yield of the crystals was 30—35 per cent. of rufigallic acid used, whilst the other compounds are in comparatively small quantity.

The author considers this reaction remarkable on account of the production of dibasic acids, the conversion of an anthracene-derivative into a body of the diphenyl series, and the formation of both hydroxybenzoic acids.

D. A. L.

Idryl. Part II. By G. GOLDSCHMIDT (*Wien. Akad. Ber.* [2 Abth.], **81**, 415—429).—This hydrocarbon, $C_{15}H_{10}$, was first described by the author, in 1877, but has since been studied by Fittig, Gebhard, and Liepmann, chiefly as to its products of oxidation.

Trichloridryl, $C_{15}H_7Cl_3$, forms nearly white needles, melting above 300° ; nearly insoluble in ether, sparingly soluble in alcohol, more readily in benzene, and easily in carbon bisulphide and xylene.

Tribromidryl, yellow, soft needles, not melting at 345° , still less soluble in solvents than the trichloride. *Dibromidryl* melts at 202° . When idryl is heated with phosphorus and hydriodic acid at 180° , it yields a hydrocarbon, $C_{15}H_{12}$, crystallising in long needles (m. p. 76°), and combining with picric acid, forming red needles

(m. p. 186°). When the action of phosphorus and hydriodic acid takes place at $240-250^{\circ}$, an oily hydrocarbon, $C_{15}H_{10}$ (b. p. $309-311^{\circ}$), is formed.

Idryl dissolves in hot concentrated sulphuric acid, with the production of *idryldisulphonic acid*, a brownish, syrupy, unstable liquid, soluble in alcohol, ether, and water. *Barium idryldisulphonate*, $C_{15}H_8(SO_3)_2Ba$, and the corresponding *calcium salt*, form yellowish crusts, soluble in alcohol. The *cadmium compound* is a yellow crystalline powder. The *potassium salt* is crystalline, and soluble in alcohol. When fused with potash, it forms a blood-red mass, dissolving in water with strong green fluorescence.

When the potassium salt is fused with potassium cyanide, it yields a crystallisable yellowish substance, melting at 220° , and a dark oil; the latter, when boiled with potash, is converted into the potassium salt of *idrylmonocarboxylic acid*, $C_{16}H_{10}O_2$ (m. p. 165°), easily soluble in alcohol and ether; little soluble in water. O. H.

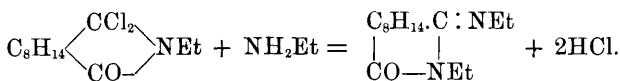
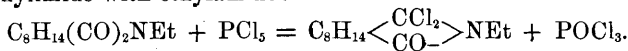
Picene. By C. GRAEBE and J. WALTER (*Ber.*, **14**, 175—178).—The hydrocarbon picene, $C_{22}H_{14}$, which Burg (*Ber.*, **13**, 1834; this volume, p. 179) extracted from lignite tar, can be obtained in large quantities by the destructive distillation of the residues from the rectification of Californian petroleum. The crude product, which melts at 250° , is purified by treatment with alcohol and carbon bisulphide, and recrystallisation from benzene; considerable difficulty is experienced in completely removing an indifferent compound containing oxygen, which exists in the crude material. Pure picene melts at 335° (corr.), and boils at 340° . W. C. W.

Essential Oil from Hemp. By L. VALENTE (*Gazzetta*, **10**, 479—481).—The essential oil from *Cannabis indica* has already been examined by Bohlig and by Personne, the latter of whom obtained from it a liquid and a solid hydrocarbon. The author has prepared the essential oil from ordinary hemp (*C. sativa*) by distilling the fresh leaves with water, and agitating the milky distillate with ether. The oil dried over calcium chloride and distilled repeatedly from sodium, is colourless and mobile (b. p. $256-258^{\circ}$). Its sp. gr. at 0° referred to water is 0.9292. The analyses agreed with the formula $C_{15}H_{24}$; the vapour-density, however, could not be determined by the ordinary methods, as it decomposes at 300° . The oil mixes in all proportions with alcohol, ether, and chloroform. Bromine acts energetically on it, forming a crystalline compound, which has not yet been investigated. Nothing at all resembling the solid hydrocarbon mentioned by Personne could be observed. C. E. G.

Amidine Bases from Dibasic Acids. By O. WALLACH and I. KAMENSKI (*Ber.*, **14**, 162—171).—*Camphorethylimidethylinidine*, $C_8H_{14} \cdot C : NEt$
 $\begin{array}{c} | \\ CO \cdot NEt \end{array}$, is formed together with camphorethylimide, $C_8H_{14}(CO)_2NEt$, by the action of phosphorus pentachloride on ethylamine camphorate (*Ber.*, **13**, 520; this Journal, 1880, Abstr., 548).

The portion of the product boiling between 284° and 286° is dissolved in absolute ether and saturated with dry hydrochloric acid gas, which precipitates the hydrochloride of the base. Camphorethylimidethylinide boils at 285° , and forms a deliquescent crystalline hydrochloride, $C_{11}H_{24}N_2O.HCl$, and a sparingly soluble crystalline hydriodide. The ethiodide crystallises in colourless long prisms which are sparingly soluble in ether, and melt at 244° with decomposition. The base is decomposed by digestion with hydrochloric acid, forming ethylamine hydrochloride and camphorethylimide (m. p. 47° , b. p. 274°).

Camphorethylimidethylinide can also be prepared synthetically by treating the product of the action of phosphoric chloride on camphorethylimide with ethylamine:—



The authors have also tried the action of phosphorus pentachloride on diethylmalonamide (m. p. 149°), dimethylsuccinamide (m. p. 175°), diethylfumaramide (m. p. 182°), ethylamine pimelate, malate, and phthalimide, also methylamine and propylamine, phthalate, and ethylphthalimide (m. p. 70°). W. C. W.

The Two Isomerides of Santonin, called Metasantonin.

By S. CANNIZZARO and G. CARNELUTTI (*Gazzetta*, **10**, 461—465).—When santonic acid is heated with hydriodic acid and amorphous phosphorus, it has been shown that, besides other substances, two crystalline isomerides of santonin are formed melting at 160.5° and 136° respectively. These may be obtained more conveniently by boiling parasantonide with hydriodic acid and phosphorus. The solution is then concentrated to remove part of the hydriodic acid, diluted with water, saturated with sodium carbonate, and agitated with ether. On evaporation, a mixture of the two metasantonins is left; these can only be separated by mechanical selection of the crystals, as their behaviour with solvents is almost identical. A mixture of the metasantonins may also be obtained by dissolving parasantonide or parasantonie acid in 10 parts of concentrated sulphuric acid, heating at 100° for two hours, diluting, neutralising with sodium carbonate, and agitating with ether.

The one metasantonin (m. p. 136°) crystallises in large monoclinic prisms which are easily powdered; the other (m. p. 160.5°) forms thin flexible plates belonging to the trimetric system. The rotatory power of both is the same.

By adding the requisite quantity of bromine to the metasantonins dissolved in chloroform, and heating until hydrobromic acid ceases to be given off, they are converted into *monobromometasantonins*, $C_{15}H_{17}BrO_3$; the one from the metasantonin of m. p. 136° forms small white crystals (m. p. 114°), very soluble in ether and in chloroform. The other, from the metasantonin of m. p. 160° , crystallises in long

silky needles (m. p. 212°), very soluble in chloroform, but only sparingly in ether. The corresponding *dibromometasantonins*, melting at 186° and 184° respectively, are produced by the continued action of bromine on the monobromo-derivatives. The first crystallises in small feathery groups of needles moderately soluble in chloroform, sparingly in ether: the second also forms colourless needles moderately soluble in both ether and chloroform. Crystalline compounds are produced by the action of chlorine on the metasantonins, but they have not as yet been studied.

C. E. G.

Action of Phosphorus Pentachloride on Santonic Acid. By S. CANNIZZARO and G. CARNELUTTI (*Gazzetta*, **10**, 459—460).—When santonic acid in chloroform solution is digested with phosphorus pentachloride, and the cold chloroform solution poured off from the excess of phosphorus pentachloride, is evaporated by passing a current of moist air over it, white crystalline crusts are formed. This substance may be purified by redissolving it in chloroform and precipitating with ether: it forms slender silky needles (m. p. about 198°) of the composition $\text{PO}(\text{C}_{15}\text{H}_{18}\text{O}_3\text{Cl})_3$. In all probability the compound $\text{PCl}_2(\text{C}_{15}\text{H}_{18}\text{O}_3\text{Cl})_3$ is first formed and is converted into the oxide by the moisture in the air. When heated with water at 120° , or when boiled with baryta-water, it gives santonic, phosphoric, and hydrochloric acids.

By the action of phosphorus tribromide on hydrosantonic acid, a well crystallised phosphorus compound is obtained, quite free from bromine.

C. E. G.

Picrotoxin. By L. BARTH and M. KRETSCHY (*Wien. Akad. Ber.* [2 Abth.], **81**, 7—44).—So-called picrotoxin can by fractional crystallisation from benzene and water be separated into at least three, and probably four, different compounds, namely, into *picrotoxin* proper, *picrotin*, and *anamirtin*.

The former constitutes about 30 per cent. of the crude picrotoxin, and is the only poisonous ingredient of the mixture. It crystallises in rhombic very brittle lustrous needles or laminæ, of a composition corresponding with the formula $\text{C}_{15}\text{H}_{16}\text{O}_6 + \text{H}_2\text{O}$, and melting at 201° with partial decomposition. It reduces silver nitrate and Fehling's solution, is intensely bitter, and highly poisonous, 0.5 mgrm. injected under the epidermis of a frog, or 1.5 to 3 mgrms. under that of a rabbit, producing poisonous effects.

Picrotin, $\text{C}_{25}\text{H}_{30}\text{O}_{12}$, forms upwards of 60 per cent. of crude picrotoxin, crystallises from water with $2\frac{1}{2}$, $3\frac{1}{2}$, and $5\frac{1}{2}$ H_2O , melts at 245° , becoming yellow, reduces silver nitrate and Fehling's solution, and is very bitter but *not* poisonous.

Anamirtin, probably $\text{C}_{19}\text{H}_{24}\text{O}_{10}$, insoluble in benzene, crystallises from water in short needles, becomes brown at 260° and black at 280° without melting. It is *neither bitter nor poisonous*, and constitutes but 2 per cent. of ordinary picrotoxin.

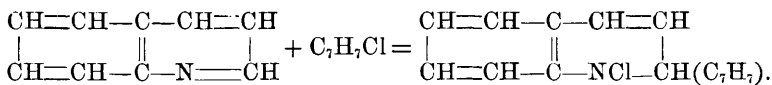
O. H.

Phytolaccic Acid. By A. TERREIL (*Compt. rend.*, **91**, 856—858). The alcoholic extract of the fruit of *Phytolacca decandra* contains the

potassium salt of a new acid to which the author gives the name of *phytolaccic acid*. The aqueous solution of potassium phytolaccate is not changed by addition of hydrochloric acid in the cold: but on warming the liquid passes into a stiff jelly which is remarkable for its solubility in strong alcohol. The isolated acid presents itself as a yellowish-brown, non-deliquescent gummy transparent varnish, very soluble in alcohol and in water. The aqueous solution is converted into jelly by strong acids. The free acid does not precipitate salts of barium or of calcium; on boiling, however, it reduces silver salts. The alkaline phytolaccates are not crystallisable. R. R.

Products from the Roasting of Coffee. By O. BERNHEIMER (*Wien. Akad. Ber.* [2 Abth.], **81**, 1032—1043).—During the roasting of coffee, water vapour is first given off, then suddenly an evolution of carbonic anhydride, and distillation of volatile substances commences. The distillate consists of an aqueous liquid and a solid part. The former contains caffeine, caffeol, acetic acid, quinol, methylamine, and acetone; the latter consists of fatty acids, chiefly palmitic. Pyrrol escapes during roasting. Of fatty acids 0·48 per cent. of the weight of the coffee employed were volatilised; of caffeine, 0·18 per cent.; and of caffeol, 0·05 per cent. O. H.

Quinoline. By A. KRAKAU (*Ber.*, **13**, 2310—2319).—Claus and Himmelmann (*Ber.*, **13**, 2045) obtained a compound of quinoline and benzyl chloride, $C_9H_7N.C_7H_7Cl$, which is decomposed by potash, forming $C_9H_7(C_7H_7)N$. The fact that the hydrochloride of this base is identical with the original addition-product, was supposed to prove the incorrectness of the generally accepted structural formula for quinoline. The author points out that the results of the late Wischnegradsky's researches (this Journal, Abstr., 1880, 269) show that this fact can be explained by the hypothesis that the double linking of the C and N atoms is destroyed.



Wischnegradsky has also shown that when cinchonine is decomposed by potash in presence of copper oxide, no evolution of hydrogen takes place, and that the quinoline formed in the reaction is not mixed with lepidine.

As the introduction of quinoline into the animal system produces a decrease of temperature, it is possible that this compound may be advantageously administered in cases of intermittent fever.

W. C. W.

Quinoline. By A. CLAUS (*Ber.*, **14**, 146—148).—In reply to Krakau's remarks (*Ber.*, **13**, 2310), the author points out that Wischnegradsky's speculations on the constitution of quinoline have not yet been supported by experimental investigation. W. C. W.

Synthesis of Quinoline. By Z. H. SKRAUP (*Wien. Akad. Ber.* [2 Abth.], **81**, 593—595).—Graebe's synthesis of alizarin-blue (dihy-

droxyanthraquinolinquinone) from nitro-alizarin and glycerol (this Journal, **36**, 259), suggested the idea that quinoline could be produced by heating a mixture of nitrobenzene, glycerol, and sulphuric acid:— $C_6H_5NO_2 + C_3H_5O_3 = C_9H_7N + 3H_2O + O_2$. The author found this to be the case, the yield, however, being very small; as it seemed probable that the excess of oxygen interfered in this reaction, aniline was employed, the reaction being for this:— $C_6H_7N + C_3H_5O_3 = C_9H_7N + 3H_2O + H_2$. He obtained the best yield, however (25 per cent.), by using a mixture of nitrobenzene and aniline.* This crude quinoline is almost pure, distilling between 227—230° (uncorr.).

In following up a reaction of Anderson's, he shows that quinoline methiodide is easily decomposed in aqueous solution by potash, even in the cold an oil separating out, whilst at higher temperatures a small quantity of a blue dye is formed. This oil commenced to distil at 240°, the greater part boiling above 300°. The composition of the lowest fraction, as found from the platinochloride, answers to lepidine, the equation, $2C_9H_7N.CH_3I + K_2O = 2C_9H_6N.CH_3 + 2KI + H_2O$, represents its production from quinoline methiodide.

D. A. L.

Lutidine Aurochloride. By O. DE CONINCK (*Bull. Soc. Chim.* [2], **34**, 634).—Lutidine aurochloride, $C_7H_9N.HCl.AuCl_3$, is decomposed by water in the same way as the platinochloride. When boiling solutions of lutidine hydrochloride and gold chloride are mixed, a red precipitate is at once formed, and, if the liquid be boiled until this precipitate just redissolves, a new salt having the composition $C_7H_9NHCl.AuCl_3 + (C_7H_9NCl)_2AuCl$, is deposited in thin red plates with a golden lustre. If the ebullition be prolonged, a deep red crystalline powder is deposited after some days. It has the composition $(C_7H_9NCl)_2AuCl$, corresponding with $(C_7H_9NCl)_2PtCl_2$.

C. H. B.

Nicotine. By A. CAHOIRS and A. ETARD (*Bull. Soc. Chim.* [2], **34**, 449—460).—The experiments described in this paper have already been published in the *Compt. rend.* and abstracted in this Journal, 1880, 672 and 815.

Cinchonine. By O. HESSE (*Annalen*, **205**, 211—217).—The author formerly assigned to cinchonine the composition $C_{20}H_{24}N_2O$, but further researches have established that the mother-liquors contain a substance which agrees with Skraup's (*Annalen*, **197**, 352) cinchonine, $C_{19}H_{22}N_2O$. It has also been shown that it is unnecessary to suppose the occurrence of two bodies, $C_{20}H_{24}N_2O$ and $C_{19}H_{22}N_2O$, which hitherto have been described under the name "Cinchonine," but now must be distinguished from one another by the names "Cinchonine and homocinchonidine." Cinchonine forms two platinochlorides, of which one (obtained by precipitating cinchonine in excess with platinic chloride without acidifying) has the composition $(C_{19}H_{22}N_2O)_2PtCl_6.H_2 + 2H_2O$, while the second by precipitating an acid solution of cinchonine has the composition $C_{19}H_{22}N_2OPtCl_6.H_2$.

* In an abstract in this Journal (**38**, 672) this method is attributed to Koenigs, although he himself (*Ber.*, **13**, 912), mentions it as Skraup's.—D. A. L.

The *neutral sulphate* forms either long needles or short thick prisms of the composition $(C_{19}H_{22}N_2O)_2H_2SO_4 \cdot 2H_2O$. The *acid sulphate* exhibits the phenomenon of supersaturation, a solution of the salt remaining for several months as a syrup, which immediately crystallises from a nucleus of the salt dropped into the solution. The salt forms either double pyramids or splendid prisms.

Contrary to the observation of Kerner the author finds that this salt is not dichroic. The optical rotatory power is found to be ($p = 10$, $t = 15$, and $l = 220$), for the sulphate $[\alpha]_D = +176.6$, and for the alkaloid $[\alpha]_D = +267.9$, whilst cinchonine prepared in another process only gave $+255.5$. The author has, however, established the identity of this alkaloid with ordinary cinchonine.

V. H. V.

Methyl-derivatives of Cinchonine. By A. CLAUS and H. MÜLLER (*Ber.*, **13**, 2290—2294).—*Cinchonine methylbromide* prepared by adding methyl bromide to an alcoholic solution of cinchonine forms four-sided crystals, containing 1 mol. H_2O , which begin to melt at 265° . This compound is easily decomposed by a solution of potash at 100° forming *methylcinchonine*, $C_{20}H_{23}MeN_2O$, which crystallises in colourless plates (m. p. 74°), insoluble in water, but soluble in ether, alcohol, chloroform, and benzene. The auro- and platinochlorides are precipitated as yellow powders, which are rapidly decomposed by sunlight in the presence of moisture. Methyl iodide combines energetically with the new base, forming needle-shaped crystals of *methylcinchonine methiodide* (m. p. 201°). *Cinchonine dimethiodide*, $C_{20}H_{24}N_2O(MeI)_2$, crystallises in plates of a yellow colour (m. p. 235°). It is soluble in alcohol and in water.

Cinchonine methyl bromide, ethyl bromide, and methylcinchonine dimethiodide were also prepared.

W. C. W.

Ethyl-derivatives of Cinchonine. By A. CLAUS and KEMPERDICK (*Ber.*, **13**, 2286—2290).—By boiling cinchonine ethiodide with a solution of potash *ethylcinchonine* is obtained as an oily liquid, which partly solidifies to a crystalline mass (m. p. 50°) after the lapse of several months. The salts of this base are deliquescent, and are obtained in the crystalline state with difficulty. The platinochloride forms microscopic plates containing $2H_2O$. It is decomposed by boiling with water. The aurochloride is precipitated as a beautiful yellow crystalline powder on the addition of gold chloride to a neutral solution of ethylcinchonine hydrochloride.

Ethyl iodide combines directly with ethylcinchonine to form ethylcinchonine ethiodide, $C_{20}H_{23}EtN_2O \cdot EtI$, crystallising in silky needles, which melt at 242° with decomposition. By boiling this compound with potash solution, *diethylcinchonine* is produced. It is insoluble in water, but dissolves freely in ether. *Cinchonine diethiodide*, $C_{20}H_{24}N_2O(EtI)_2$, prepared by the action of ethyl iodide on the monoethyl-compound, or by the action of an excess of ethyl iodide on cinchonine at 150° , crystallises in prisms of a dark yellow colour, which contain 1 mol. H_2O . The crystals melt with decomposition at 264° ; they are more soluble in water, and less soluble in ether than

the monethiodide. By boiling with potash, a resinous base is formed soluble in ether.

The addition of ammonia to the diethiodide produces in the course of 12 hours a crystalline precipitate, which appears to consist of a mixture of two bases. W. C. W.

Benzyl-derivatives of Cinchonine. By A. CLAUS and W. TREUPEL (*Ber.*, **13**, 2294—2297).—*Cinchonine benzyl chloride*, $C_{26}H_{24}N_2O.C_7H_7Cl$, is formed together with cinchonine hydrochloride and a red colouring matter when benzyl chloride is boiled with twice its weight of cinchonine dissolved in alcohol. On evaporating the alcoholic solution, a crystalline mass remains, from which the cinchonine benzylchloride can be obtained by removing the cinchonine hydrochloride by repeated washing with cold water and recrystallising the residue, or the whole mass may be dissolved in hot water, the cinchonine precipitated with ammonia, the colouring matter removed by boiling with animal charcoal, and the cinchonine benzylchloride in the filtrate separated from ammonium chloride by repeated recrystallisation. Cinchonine benzylchloride crystallises in lustrous needles (m. p. 248°), soluble in alcohol and hot water. Platinum chloride produces a yellow crystalline precipitate in the aqueous solution. *Benzylcinchonine* formed by the action of a solution of potash on the chloride crystallises in colourless needles (m. p. 117°), soluble in alcohol, ether, and benzene. The single salts of this base are non-crystallisable syrups. The platinochloride is crystalline. *Benzylcinchonine benzylchloride*, produced together with benzylcinchonine hydrochloride and a red colouring matter, by boiling an alcoholic solution of benzyl cinchonine with benzyl chloride, forms colourless crystals, soluble in alcohol and in water; they melt at 255° with decomposition.

Cinchonine benzylhydrate is prepared by the action of moist oxide of silver on cinchonine benzylchloride. The hydrochloride of this base is identical with cinchonine benzylchloride. W. C. W.

Cinchomeronic Acid. By Z. H. SKRAUP (*Wien. Akad. Ber.* [2], **81**, 337—345).—The author believed that the pyridine- γ -monocarboxylic acid which was prepared by him by oxidising cinchonic acid, contained traces of a dicarboxylic acid, and he instituted this research to prepare it and study its compounds. He heats air-dried pyridinetri-carboxylic acid in quantities of 5 grams in flat basins at 120 — 125° C, until the loss in weight is equal to that required for the expulsion of 1 mol. of carbonic anhydride and the water of crystallisation. A small quantity of the monocarboxylic acid is formed in the reaction. The dicarboxylic acid, $C_7H_5NO_4$, is extracted from the product by hydrochloric acid, from which it crystallises in long prisms. It melts and decomposes at 158 — 159° . With the exception of the higher melting point, its properties are identical with those of Weidel's cinchomeronic acid. The *normal sodium salt*, $C_7H_3Na_2NO_4 + 2H_2O$, crystallises in clear plates. The *acid sodium salt*, $C_7H_4NaNO_4$, is obtained by dissolving a weighed quantity of the acid in a solution of the theoretical amount of normal salt. It crystallises in granular

anhydrous masses. The *normal calcium salt*, $C_7H_5CaNO_4 + 3H_2O$, is obtained by neutralising the acid with ammonia, and then adding calcium chloride. It forms clear prismatic monoclinic crystals. Hoogenwerff and van Dorp found that the calcium salt of their acid, which was doubtless identical with cinchomeric acid, contained $3\frac{1}{2} OH_2$.

The Copper Salt.—The author explains the discrepancy between the observations of Hoogenwerff and van Dorp and those of Weidel by the statement that if the copper salt is precipitated from a hot solution with excess of copper acetate and boiled for a longer time, it does not disappear. The *hydrochloric acid compound*, $C_7H_5NO_4 + HCl$, obtained by gently warming the solution of the acid with concentrated hydrochloric acid, or by acting on the solid substance with hydrochloric acid, is decomposed on adding a large quantity of water. It dissolves easily in a small quantity of boiling water, and crystallises from the solution unchanged in short, thick, monoclinic prisms. The *platinochloride*, $(C_7H_5NO_4)_2H_2PtCl_6$, is obtained in yellow plates when the hydrochloric acid compound is dissolved in water, with addition of as small a quantity of hydrochloric acid as possible, platinum chloride added, and the solution allowed to stand over sulphuric acid. He observed that on being allowed to stand over sulphuric acid for eight days, the salt appeared to lose $2HCl$.

J. I. W.

Cinchonidine and Homocinchonidine. By O. HESSE (*Annalen*, **205**, 194—211).—The author has established that the mother-liquors of cinchonidine sulphate is separated by fractional crystallisation into two portions, of which one agrees with Winkler's quinidine sulphate, but the second portion is distinctly different. The author has also compared Koch's cinchonidine and quinidine (*Pharm. Post*, **10**, 208), and has found that the former agrees with the second fraction alone, whilst Koch's quinidine agrees with the author's cinchonidine sulphate. In order to distinguish this alkaloid, it has been named homocinchonidine (*ὁμοκιν*, cinchonidine). Further researches have shown that homocinchonidine sulphate when mixed with quinine sulphate does not crystallise in the form of homocinchonidine, but in the form of cinchonidine sulphate.

PART I. Cinchonidine.—The author has modified his process of preparing cinchonidine. A dilute aqueous solution of its sulphate is precipitated by ammonia, the precipitate is then dissolved in hot alcohol, and this latter on evaporation gives crystals of cinchonidine and homocinchonidine, whilst the quinine remains dissolved. The cinchonidine and homocinchonidine may be separated by fractional crystallisation from the aqueous solutions of their sulphates. Cinchonidine is pure when (1) its solution in excess of dilute sulphuric acid gives no fluorescence; (2) it melts at $200^\circ C$.; (3) its neutral sulphate crystallises out from a solution in hot water (1 : 50) in the form of glistening needles.

The author assigned the formula $C_{20}H_{24}N_2O$ to cinchonidine sulphate; he now changes it to $C_{19}H_{22}N_2O$, although his combustion analyses agree better with the former than with the latter formula.

Cinchonidine dissolves in ether (sp. gr. 72) in the ratio 1 : 188, in

alcohol (97 per cent.) in the ratio 1 : 16·3. In the optical rotatory power ($p = 4$, $t = 15$), in chloroform solution $[\alpha]_D = -70\cdot0$, for solution in dilute hydrochloric acid ($p = 5$) $[\alpha]_D = -174\cdot6$. Cinchonidine hydrochloride forms dark octohedral crystals containing 1 mol. H_2O . From analyses of the hydrochloride, platinochloride, neutral sulphate, and from the fact that cinchonidine when treated with hydrochloric acid is converted into apocinchonidine, $C_{19}H_{22}N_2O$, without formation of methyl chloride, the formula $C_{19}H_{22}N_2O$ is established for cinchonidine.

By varying the conditions neutral cinchonidine sulphate crystallises out from its aqueous solution with 6, 5, or 2 mols. H_2O .

Cinchonidine quinate is formed by the direct action of cinchonidine and quinic acid; it crystallises in glistening needles.

Cinchonidine salicylate crystallises in colourless needles with composition $C_{19}H_{22}N_2O \cdot C_7H_6O_3$.

PART II. *Homocinchonidine* (cinchonidine of Skraup and Vortmann, Koch, Kerner).—This alkaloid accompanies cinchonidine in many cinchona barks; it passes into the dark sulphate mother-liquors in the quinine manufacture. Homocinchonidine crystallises from alcohol in dark anhydrous prisms, but from a dilute solution in leaflets; it dissolves in chloroform, but is almost insoluble in water. Its alcoholic solution is strongly alkaline. For its optical rotatory power the author finds in alcohol solution ($p = 2$) $[\alpha]_D = -107\cdot3$, for chloroform solution ($p = 4$) $[\alpha]_D = -70\cdot0$, for hydrochloric acid solution $[\alpha]_D = -167\cdot9$. Homocinchonidine melts at 205° ; its solution in excess of dilute sulphuric acid gives no fluorescence, and its alcoholic solution with chlorine and ammonia gives no coloration. Its formula is $C_{19}H_{22}N_2O$. Neutral hydrochloride of homocinchonidine crystallises in rhombic octohedra, containing 1 mol. H_2O , or from a concentrated solution with 2 mols. H_2O . The platinochloride forms an orange-yellow crystalline powder. The hydriodide, sulphocyanide, and nitrate crystallise in colourless prisms, the tartrate and thiosulphate in colourless needles. The neutral sulphate crystallises from hot water in white needles with 6 mols. H_2O . From strong concentrated aqueous solutions of the sulphate, the salt separates out in a thick mass, which after drying resembles magnesia, and it is this form which occurs in commerce.

Neutral homocinchonidine phenyl sulphate crystallises in glistening needles, the acid sulphate in colourless prisms, and the quinate in white needles. The author's researches have established that it is not possible to convert cinchonidine and homocinchonidine one into the other, and that these alkaloids are different in their properties.

V. H. V.

Chlorinated Derivatives of Strychnine. By C. RICHET and G. BOUCHARDAT (*Compt. rend.*, **91**, 990—993).—Monochlorostrychnine, $C_{24}H_{21}ClN_2O_4$, is formed by passing the theoretical quantity of chlorine into a solution of strychnine hydrochloride; it may be purified from higher chlorinated derivatives by conversion into the sulphate and recrystallisation. The base is crystalline and very soluble in chloroform, ether, and alcohol. Monochlorostrychnine is capable of fixing 3 mols. H_2O , forming a chlorinated derivative analogous to tri-

hydrostrychnine. These compounds possess many of the properties of the alkaloid. The preparation of trichlorinated strychnine, $C_{42}H_{19}Cl_3N_2O_4$, and that of trichlorinated hydrostrychnine are also described. These substances have colour reactions and other properties essentially different from those of the monochlorinated compounds, being, for instance, almost without physiological action in a dose of 0.5 gram. Another chlorinated derivative described by the author had a composition corresponding with $C_{42}H_2Cl_{20}N_2O_4$.

R. R.

Alkaloids from Belladonna and Datura Stramonium. By E. SCHMIDT (*Ber.*, **14**, 154—157).—The crude alkaloid from the roots of the belladonna contains hyoscyamine and atropine; the crude alkaloid from the seed of *Datura stramonium* contains atropine, daturine, and hyoscyamine. After recrystallising the impure alkaloids from dilute alcohol, tropine is found in the mother-liquor. Atropine and daturine platinochlorides crystallise in the monoclinic system and are isomorphous. Tropine platinochloride also crystallises in this system. Hyoscyamine platinochloride crystallises in the triclinic system.

W. C. W.

Atropine. By L. PESCI (*Gazzetta*, **10**, 425—430).—The atropine was prepared from dry belladonna leaves by exhausting them with cold water, evaporating the extract at a gentle heat, and, after mixing the syrupy mass with soda solution, agitating with benzene to extract the alkaloid. The benzene solution was then agitated with dilute sulphuric acid, and the acid solution after addition of an alkali was in like manner agitated with chloroform. On mixing the chloroform solution with an equal volume of light petroleum (benzolene), and allowing it to evaporate spontaneously, the liquid soon becomes filled with long colourless needles of pure atropine. The mother-liquors contain a small quantity of another alkaloid. Pure atropine, $C_{17}H_{23}NO_3$, melts at $106-108^\circ$. A table of its reactions is given; with picric acid it produces a yellow precipitate even in presence of sulphuric acid; with concentrated sulphuric acid no coloration in the cold, but a yellow tinge appears on heating; on adding water a pleasant odour of roses is evolved.

Atropine is not altered by boiling with a saturated solution of tartaric acid.

Action of Nitric Acid on Atropine.—If atropine is strongly heated with nitric acid, it yields picric acid, but if it is gradually added to fuming nitric acid, maintained at about 50° , it dissolves with a slight yellow coloration which subsequently disappears. On neutralising the product and extracting with ether, an oily base is obtained soluble in chloroform. With dilute sulphuric acid, it yields a crystalline sulphate having an odour of hawthorn; the sulphate is readily soluble in boiling water, but only sparingly in the cold. The *platinochloride* is crystalline, and, unlike that of atropine, is but sparingly soluble in hydrochloric acid. The *aurochloride* is a yellow amorphous precipitate, whilst that of atropine crystallises readily in tufts of needles. There are also many other points of difference in its reactions from those of atropine. In its physiological effects, it does not cause dilation of the pupil, and it does not appear to be poisonous.

C. E. G.

Gelatin dried at 130° resists solution in water, but treatment with acids and heating with water at 120° restores it to its original state.

E. W. P.

Dry Distillation of Gelatin. By H. WEIDEL and G. L. CIAMICIAN (*Wien. Akad. Ber.* [2 Abth.], **81**, 512—530).—The authors heat gelatin in portions of 200 grams in an iron retort, and collect the distillate in three portions, A, B, and C.

The portion A consists mainly of a crystalline substance which, when purified by recrystallisation first from glacial acetic acid, and then from chloroform, is obtained in almost colourless pearly plates. It melts at 268 — 269° C., and can be sublimed. Its vapour-density is 6.2. The authors propose to call it pyrocoll, because of its mode of formation from gelatin. They give to it the formula $C_{10}H_8N_2O_2$. By boiling it with potash solution, carbopyrrolic acid is formed. The authors obtained this acid in large colourless monoclinic crystals. Its formation from pyrocoll is shown by the equation $C_{10}H_8N_2O_2 + 2KOH = 2C_5H_4KNO_2$. *The barium salt*, $C_{10}H_8BaN_2O_4$, of carbopyrrolic acid is prepared by neutralising it with baryta solution and precipitating the excess of baryta with carbonic anhydride. It forms thin white silky plates. *The ammonium salt*, $C_5H_4NH_4NO_2$, crystallises in rhombic prisms.

When pyrocoll is heated in sealed tubes at 100° for some hours with saturated alcoholic ammonia, it is converted into carbopyrrolamide. It crystallises in well-formed tabular monoclinic crystals. By heating pyrocoll with zinc-dust in a current of hydrogen, an oil, smelling like chloroform, is obtained: the quantity was not sufficient for analysis. The authors conclude that pyrocoll is a derivative of pyrrol. The formation of carbopyrrolic acid, if the molecule were only half so great, would be analogous to the conversion of a "lactide" anhydride into the corresponding acid,—isatin into isatinic acid, for instance. Attempts to prepare pyrocoll synthetically from carbopyrrolic acid, by combining 2 mols. with elimination of 1 mol. of water, proved failures.

The portion B consists of oily products, which may be separated by fractionating into portions, boiling at 130° C., at 140 — 150° C., and at 160 — 170° C. respectively. The other fractions were not obtained in quantity sufficient for the authors to determine their constitution. On treating the first fraction with potassium and afterwards with water, pyrrol (b. p. 127°) was obtained, whilst the second fraction gave homopyrrol, C_5H_7N (b. p. 145°). The fraction which boils at 160 — 170° gives dimethylpyrrol, C_6H_9N .

The portion C consists of the light products mixed with water. It contains principally methylamine and butylamine, and perhaps a trace of quinoline.

J. I. W.

Physiological Chemistry.

Action of Acid Gastric Juice on the Nitrogenous Constituents of Fodder. By A. STUTZER (*Bied. Centr.*, 1880, 731—734).—The acid gastric juice was prepared by treating the inner skin of a pig's stomach for 12 hours, with the third part of 5 litres water acidified with 50 c.c. hydrochloric acid. This solution was then nearly neutralised with sodium carbonate, leaving 1—2 per cent. of free acid. Fodder of different kinds was digested for 10—12 hours at a temperature of 40° in the acid solution obtained as above. The results were, that a greater portion of the albuminoids were dissolved, but a portion still remained unacted on; this appears to be a new fact; so that vegetable foods resemble animal substances in that they contain an insoluble albuminoid containing phosphorus, which may also be called "nuclein." A few of the results are shown in the following table:—

	Total N.	In percentage of total N.		
		Non-albuminous nitrogen.	Digestible nitrogen.	Indigestible.
Poppy cake	6·215	5·6	82·2	12·2
Rape „	5·364	13·3	73·7	13·0
Palm „	2·721	0	78·0	22·2
Oats	1·556	4·1	84·1	11·8
Potatoes	1·520	49·93	43·63	6·44
„	1·313	26·73	58·65	14·62
Lucerne hay	2·549	28·20	50·27	21·53

Cow's milk is wholly digestible, but the nitrogenous compounds in peat are insoluble. E. W. P.

Researches on the Digestion of Proteïds. By O. KELLNER (*Bied. Centr.*, 1880, 763—765).—In a former communication (this Journal, 1880, 563), it is shown that the amount of nitrogen excreted as taurine, &c., is proportional to the amount of dry matter digested, and that easily digested foods, although poor in proteïds, have a considerable influence on the coefficient of digestion of the crude proteïds. A further set of experiments has corroborated these deductions. Rice starch increases the nitrogenous biliary secretions in a direct ratio. Comparison of the author's experiments with those of Stutzer, in which poppy cake was dissolved by gastric juice, show that the figures obtained in the latter case lie higher than those obtained by direct experiment on the animal, and are so much higher the smaller the quantity of digestible nitrogenous matter, and the higher the amount of digestible dry matter, is in the food given:—

	Nitrogen in dry matter, per cent.	Coefficient of digestion.		
		Dry matter, animal.	Crude protein.	
			In the animal.	By gastric juice.
Wheat straw.....	0·536	45·0	14·3	41·9
Meadow hay.....	1·705	54·5	54·7	64·9
Sesame cake.....	7·855	69·3	90·3	94·1
Barley	2·347	83·5	80·3	95·0

Of 100 parts of the dry matter, the gastric juice prepared by Stutzer digests a larger quantity than the animal, the difference being represented by the following figures:—Wheat straw, 0·153; hay, 0·174; sesame, 0·298; barley, 0·345; and these percentages, calculated in 100 parts of digestible dry matter, may be considered in round numbers to be 0·4 nitrogen. This quantity is but slightly altered by the kind of food given; much indigestible fibre slightly lowers it, whereas easily digested food raises it; it therefore approximately represents the absolute value by which the digestion of proteids is lowered by 100 parts of gluten, flesh-meal, sugar, and mucilage. It may be taken for granted that 0·3—0·5 per cent. of nitrogen corresponds with that quantity of nitrogenous secretions which are removed, together with the undigested matter in the fæces, by the digestion of 100 parts of fodder.

E. W. P.

Feeding Cows with Rice Meal. By M. SCHRODT and others (*Bied. Centr.*, 1880, 734—737).—During the first period of the experiment, the cows were fed on 5 kilos. hay, 2 of oat straw, 5 of turnips, 3 of rye and wheat bran, 1 of rape cake, and 20 grams salt per day; during the second period, half the bran was replaced by as much rice meal; in the third period, half the bran was replaced by 2·5 rice meal, and the rape cake was not given. The nutrient ratio of the above mixtures was as follows:—Periods 1 and 2, 1 : 1·51; period 3, 1 : 1·64. The cows to all appearance flourished and were healthy, but their live-weight decreased steadily. The effect of the rice on the yield of milk was, up to the end of period 2, good; but when the bran was no longer given (during a sub-period), the yield was still increased, but only to a small extent, and the butter was soft. During the succeeding periods the rice was found to be prejudicial to the yield of milk, therefore, although a small addition of rice meal is to be recommended, a large quantity is of no use.

E. W. P.

Results of Fattening Calves with Skim Milk. By H. BECK-HUSEN (*Bied. Centr.*, 1880, 737—739).—Thirty young calves were fattened with skim milk. The experiments were instituted to determine whether there was a gain by so doing. The results were as follows:—The daily increase in weight of the calves was 0·69—1·6 kilos., and to produce 1 kilo. live-weight 6·1—28·9 kilos. milk were necessary. The length of time necessary for fattening had great influence on the amount of milk required to produce 1 kilo. live-weight,

thus a period of 20—30 days required 7·9 litres, whereas a period of 80—90 days required 20·05 litres, so that the further the process of fattening had proceeded, so much the more was the value of the milk as food reduced, although the fatter beast brought a higher price.

E. W. P.

Incompletely Oxidised Sulphur in the Urine. By R. LÉPINE and FLAVARD (*Compt. rend.*, **91**, 1074).—In the urine of patients suffering from certain diseases of the liver, the authors have found in some cases as much as 40 per cent. of the total sulphur present to exist in a state of oxidation inferior to that of sulphuric acid.

R. R.

Formation of Free Sulphuric Acid in the Gastropoda, especially Dolium Galea. By R. MALY (*Wien. Akad. Ber.*, [2], **81**, 376—386).—In the Prosobranchia there are two salivary glands situated near the alimentary canal at the back of the throat. In *Dolium cassis* and *triton*, the glands have a different construction, inasmuch as they are divided into two portions, a small forepart, which is solid, and a larger hind one, which is of a slimy nature. The latter hardly resembles a gland, as it is composed of an aggregation of membranes. The saliva of *Dolium galea* is a colourless, slightly opalescent liquid, which reddens litmus. When it is evaporated with a trace of sugar, a blackening is readily produced. The author finds it to contain 0·98 per cent. of sulphuric acid. He thought it probable at first that this free acid was formed in an analogous manner to that in which hydrochloric acid is produced in the gastric juice of higher animals, in this case according to the equations (1) $\text{CaSO}_4 + \text{Na}_2\text{HPO}_4 = \text{CaHPO}_4 + \text{Na}_2\text{SO}_4$; (2) $2\text{CaHPO}_4 + \text{CaSO}_4 = \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{SO}_4$. He made several experiments in order to prove this hypothesis; but found the acid is set free only on boiling, and that it is phosphoric acid, and not sulphuric.

The author next looked for oxalic acid in the animal, then for alumina or some unoxidised sulphur compound; but could not detect any of them. He also proved that the sulphate could not be decomposed by carbonic acid under pressure, nor could the free acid be formed together with dolomite. He likewise states that the saliva contains no pepsin.

J. I. W.

Physiological and Physiologicochemical Effects of Quinoline. By J. DONATH (*Ber.*, **14**, 178—187).—A subcutaneous injection of 0·25 gram of quinoline hydrochloride produced a diminution of temperature of 1·5° for 2½ hours in a strong rabbit. The rate of respiration also diminished.

A dilute solution (0·2—0·4 per cent.) of quinoline hydrochloride prevents lactic fermentation, and the decomposition of urine and glue; it also delays the coagulation of milk and of blood. It does not, however, interfere with alcoholic fermentation.

W. C. W.

Chemistry of Vegetable Physiology and Agriculture.

Nutrition of the Lower Orders of Fungi by Carbonaceous and Nitrogenous Matter. By V. NÄGELI and O. LOEW (*Bied. Centr.*, 1880, 760).—Of all the substances which will support the growth of the lower orders of fungi, amides and amines appear to be the most suitable; moreover, all ammonia salts, and for a few fungi, nitrates are capable of providing food. But nitrogen in the free state is not assimilated, neither that from cyanogen nor cyanides; if cyanogen at any time is available, it is because ammonia is produced by the action of hydrogen set free by the fermentation. Mildew and schizomycetes are capable of assimilating nitric acid, whereas bacteria cannot. Carbon can be readily assimilated from a great number of organic compounds; in the case of mildew the solutions became acid, whilst with the schizomycetes the solutions become alkaline. In fact nearly all carbonaceous matter, so long as it is soluble, and oxygen has free access, will support the life of these fungi; they will even form in alcohol, acetic acid, phenol, salicylic, and benzoic acids, whereas they die in solutions of urea, oxalic and formic acids, and oxamide.

E. W. P.

Growth of Yellow Lupines. By E. WEIN (*Landw. Versuchs.-Stat.*, 26, 191—206).—An examination of these plants at four different stages of their growth, was instituted for the purpose of ascertaining the absolute and relative quantities of their organic and mineral constituents at these various stages. The seeds were sown on the 6th of May, and samples of the plants were taken and examined on July 1st, July 22nd, August 24th, and September 24th respectively. The plants were taken whole out of the earth, cleaned, and air-dried before analysis.

100 plants were found to contain—

	At end of period			
	1.	2.	3.	4.
A. Parts above ground :—	grams.	grams.	grams.	grams.
Nitrogenous substance .	88·59	183·58	469·14	445·00
Nitrogen-free extract ..	126·94	262·93	909·77	888·31
Fat	3·84	8·83	37·06	55·62
Fibre.....	60·99	159·38	796·46	891·94
Ash	34·33	59·46	162·95	137·61
B. Roots :—				
Nitrogenous substance .	17·32	22·53	33·60	31·79
Nitrogen-free extract ..	19·02	44·25	81·60	96·89
Fat	0·69	1·41	3·24	3·65
Fibre.....	18·28	39·34	79·10	116·67
Ash	4·49	8·03	14·18	15·73

From the above tables it will be seen that lupines are in their earlier stages of growth relatively richer in nitrogen, nitrogen-free extract,

and mineral matter, than they are at later periods, the reverse occurring in the case of fat and woody fibre; whilst in the roots the same law holds, except in the case of the extract and fat, the proportions of which increase up to the blossoming period, and then diminish, as in the rest of the plant. The greatest activity of vegetable growth is exhibited in the blossoming period, which lies between stages 2 and 3; during this time, the largest quantity of organic matter is produced. After the blossoming season, assimilation of material from the soil, whether organic or inorganic, may be said to have stopped; an increase of woody fibre is, indeed, observed in the fourth period, but this occurs partly at the expense of other organic constituents.

J. K. C.

Influence produced on the Growth of the Plant by previously Steeping the Seed. By C. KRAUS (*Bied. Centr.*, 1880, 746—748).—Seeds which had been steeped for 24 hours previous to sowing were found to sprout earliest; but if after soaking they were dried, then they sprouted last, as compared with normal seed. Prepared seeds grow most rapidly, and continue to grow longer than the unprepared seed. Plants grown from soaked seeds were found to be most fertile; those seeds which, after soaking had been dried, ranking next.

E. W. P.

Injurious Effect of Kainite and Superphosphate on the Germination of Potatoes. By M. FLEISCHER (*Bied. Centr.*, 1880, 765—767).—Manuring with the above manures appears to increase the amount of ash in the tuber from 3·77 per cent. (normal amount) to 7·93 per cent., and to introduce generally in the ash an abnormal quantity of those substances contained in the manures. Comparing the analysis of the ash of normal and damaged potatoes with the composition of kainite, we find:—

	Normal.	Damaged.	Kainite.
K ₂ O.....	60·4	46·76	16·0
Na ₂ O	2·6	6·14	78·6
MgO	4·7	2·68	13·2
SO ₃	6·5	12·44	26·6
Cl.....	3·1	19·52	33·1

Why magnesia is an exception is not as yet explained. When superphosphate is employed, the amount of phosphoric acid in the ash is nearly doubled.

E. W. P.

Comparison of Diseased and Sound Lemon Trees. By L. RICCIARDI (*Gazzetta*, 10, 443—459).—The lemon trees in Sicily for some time past have been affected by a disease called “gomma” (gum), and now they are attacked by another, the “pidocchio” (*Mythylapsis flavescens*). In order to ascertain if these diseases depended on the relation of the mineral constituents, the author has undertaken an extended series of analyses, comprising the physical properties and chemical constituents of the soil, the composition of the ash of the trunk, leaves, and different parts of the fruit of sound

and diseased trees, and the average weight of the leaves and fruit, and of the rind, juice, and seeds of the fruit. The only marked difference between the sound and affected plants is, that the quantity of potassium in the latter is smaller; but whether this diminution is caused by the disease, or the disease is due to want of assimilable potash in the soil, has not been determined. The author suggests that potassium sulphate should be tried as a manure. C. E. G.

Cultivation of several Varieties of Potatoes. By F. HEINE (*Bied. Centr.*, 1880, 753—756).—A report on the yield of several varieties of potatoes and of the amount of starch which they contain. It is found that the best sort, taking both the yield and starch into consideration, is Eos, then come Aurora, Alcohol. Others, which are lower in yield, but very high in starch, are Achilles, Ceres; while Richter's Emperor, Early Rose, &c., are remarkable for very heavy yield, but with a medium amount of starch. E. W. P.

Analysis of Cocoa and Palm Nut Meal. By A. PETERMANN (*Bied. Centr.*, 1880, 731).

	Cocoa nut.	Palm nut.
Water.....	13·11	10·59
Albuminoïds.....	19·16	14·98
Fat.....	6·70	5·08
Digest. cell., &c.	43·91	50·49
Fibre.....	7·40	15·05
Ash.....	9·72	3·81
Nutrient ratio	1 : 3·16	1 : 4·22

E. W. P.

Experiments on Sugar-beet. By G. KLEIN (*Bied. Centr.*, 1880, 773).—It being uncertain whether the climate of East Prussia was favourable to the cultivation of the sugar-beet, 51 sets of experiments were made in different places. The average yield was (per morgen) 7,800 kilos.; average weight per root, 840 grams; amount of sugar in whole beetroot, 13·3 per cent.; sugar in juice, 14 per cent. Soluble phosphate was found to be the best manure, either alone or mixed with ammonium sulphate; those roots were richest in sugar which remained longest in the ground. E. W. P.

Composition of "Diffusion" and "Press" Residues. By A. PETERMANN (*Bied. Centr.*, 1880, 729—731).—The amount of the feeding materials in the above residues from beet is as follows :—

	Water.	Albumin.	Fat.	Dig. cell., &c.
Diffusion residue.....	89·91	1·08	0·08	6·13
" " dry.....	—	10·70	0·79	61·76
Press residue.....	72·48	2·18	0·3	15·98
" " dry.....	—	7·92	1·09	58·08

It is evident that the "diffusion" residue is a more watery and

poorer food than the other, yet the nutrient ratio is better, being 1 : 5.9; whereas that of the "press" residue is 1 : 7.7. E. W. P.

Changes produced in Beet-leaves by Fermentation. By O. KELLNER (*Bied. Centr.*, 1880, 724—729).—A large quantity of beet-root leaves were allowed to rot in pits, some of them being enclosed in air-tight glass vessels, so as to estimate the effects produced by simple fermentation. After six months it was found that the leaves in the glass contained 8.44, and the others 13.86 per cent. of dry matter; whereas the fresh leaves contained 10.54: of the dry matter those in the glass had lost 18.00; the others, which had been pressed, 49.36 per cent. No other feeding material loses so much by storing as these leaves. Sainfoin of its 16.8 per cent. dry matter only loses 24 per cent. when kept for eight weeks. Of volatile acids, reckoned as acetic acid, 0.67 per cent. were found; of non-volatile acids reckoned as lactic acid, 2.99 per cent. were found. From the analyses of the fresh and fermented leaves, the results of which are given in tabular form, it would seem that the most important change is the loss of mineral matter. The nitrogenous matter undergoes considerable alteration, and the nitrates are destroyed.

It is therefore evident that simple fermentation causes a very considerable change in the composition of the leaf, and that when some of the soluble substances are removed, by pressure, &c., as occurs when the leaves are piled, the change is greater. The alteration in the fibre is the same in both cases, so that in both the fermentation action is the same, and the fat does not appear to have been altered to any extent.

Of the mineral constituents, great loss of potash, magnesia, phosphoric and silicic acid, and chlorine occurred; the soluble oxalates were also removed, being reduced from 1.44 to 0.55 per cent. The partial removal of the bases and oxalates accounts for the fact that beet-leaves are comparatively harmless to cattle after they have been allowed partly to decay. E. W. P.

Flesh-meal as Fodder. By A. KELLER-EBERSTADT (*Bied. Centr.*, 1880, 770).—The following mixture is recommended for fowls:—2 kilos. crushed maize, $\frac{1}{4}$ kilo. flesh-meal, $1\frac{1}{2}$ kilos. malt-coombing; this mixture to be pulped with 1—2 kilos. boiled potatoes.

E. W. P.

Preparation of Food for Pigs. By H. J. MENDEL (*Bied. Centr.*, 1880, 771).—The result of feeding pigs with boiled maize, maize crushed and boiled, and raw maize, were that the animals increased most when the maize was crushed and boiled.

E. W. P.

Permeability of Soils to Air. By G. AMMON (*Bied. Centr.*, 1880, 706—710).—With coarse soils, the permeability is inversely proportional to the height of the column of soil; with fine-grained soils, the amount of air which passes is in a rather less proportion. Of the various soils, powdered clay is the least pervious to air, whereas sandy soils are most so. The presence of water reduces the permeability of the soil, and this reduction is higher as the amount of

water increases; but if only a small amount of moisture is present, then the permeability is raised, which is explained by the fact that the grains of sand present unite to form larger grains, and this renders the soil more open. Frost reduces the permeability, the reduction being dependent on the amount of water present. The permeability of a dry soil for moist air is higher than for dry air, and that of a moist soil is lower for moist than for dry air. E. W. P.

Percolation of Water through Soils. By F. SEELHEIM (*Zeits. Anal. Chem.*, 1880, 387—418).—The author has taken up the subject where it has been left by Darcy, Hagen, and by P. Harting. He separately examined most carefully pure sand, pure clay, and calcium carbonate. The sand had been freed from calcium carbonate and from clay by treatment with hydrochloric acid, and by fusion with acid potassium sulphate; the clay had been treated alternately with acids and with alkalis, and had a composition corresponding with the formula $\text{Al}_2\text{O}_3, 2\text{SiO}_2 + 2\cdot3\text{H}_2\text{O}$; the calcium carbonate had been obtained from chalk by treatment with potash and by levigation.

It was found that the weight of a certain bulk of sand is independent of the size of the particles, and that the interstices between the particles are always of equal aggregate volume. Under the same conditions, the volume of water passing through a certain bulk of sand was always the same. The volumes were directly proportional to the total water-pressure, adding the height of the column of sand to the height of the column of water, no portion of the pressure being neutralised by capillarity, unless the surface of the water lies within the column of sand. The volumes are inversely proportional to the depth of the stratum of sand, but are independent of the diameter of the tubes used in the experiment. The temperature of the water has a considerable influence on the amount of percolating water. Thus in 15 minutes through one of the tubes there passed at $9^\circ 94$ c.c.; at 12° , 100 c.c.; at 19° , 120 c.c., the formula $Q = 79\cdot346 (1 + 0\cdot0136t + 0\cdot000704t^2)$ expressing the general ratio.

The volume of water percolating is in proportion to the square of the radius of the particles of sand. The size of the smallest particles was determined as follows: 0·2 gram of sand was fused with 20 grams of potassium dichromate. After cooling, this melt readily forms a homogeneous powder, containing the sand equally divided, because the sp. gr. of the sand is almost identical with that of the dichromate. A weighed quantity of the powder is treated with water, and the sand-grains are counted on a plate of glass divided into a number of squares.

If a number of strata of sand of different degrees of fineness are placed one above the other, the volume of the percolating water is only regulated by the stratum of the smallest particles, the coarser particles not coming into account, but if a mixture of sand of various sized grains is used, the permeability is equal to the mean of that of the grains of the several sizes, provided the smallest particles are not small enough to find room between the interstices of the larger ones. If these be small enough to find room in the interstices, then the permeability is about 1·2 times larger than that of the fine sand taken by

itself. Air bubbles between the sand grains act precisely like small sand particles.

Experiments with clay have shown that finely divided clay is deposited from water in layers, of which the lower contains less water than the upper, and that further subsidence takes place even after some months. The subsidence is quite independent of the pressure of the water. Moist clay, containing water and clay in the proportion of 1 : 3 in layers of 1.5 millimetres is absolutely impervious to water under a pressure of 1.5 metres, but pervious at higher pressures.

The author finds also in the case of clay and of chalk, that the volume of percolating water is proportional to the height of the column of water, inversely proportional to the depth of the stratum of clay or chalk, and dependent on the temperature of the water, the formula $Q = 0.714 (1 - 0.00224t + 0.002038t^2)$, expressing the relation of the temperature in the case of clay, and the formula,

$$Q = 0.781 (1 + 0.093t + 0.00005t^2),$$

in that of chalk.

The author has further examined the laws of percolation in the case of mixtures of clay and chalk, of sand and clay, of sand and chalk, and of sand, clay, and chalk, and he finds that these laws are similar to those observed in the case of the pure soil constituents when taken separately.

He draws the following practical conclusions from the results of his experiments.

To determine the permeability of water of any district under given conditions, only the stratum made up by the smallest particles need be taken into account, no matter in what order the strata may be superimposed.

Experiments on a large scale do not furnish any measures of the permeability of any soil, unless the composition of the soil is known; the thickest stratum of sand allowing the passage of many hundred times more water than a layer of clay only 1 cm. in thickness.

In the case of dykes, the permeability may be regulated by inserting layers of clay between layers of sand. If the dyke is built upon sand, the stratum of clay must be continued to a certain depth depending on the nature of the sand.

O. H.

Artificial Manures. By DÜNKELBERG and others (*Dingl. polyt. J.*, 237, 459—465).—It is asserted that phosphates capable of being dissolved by ammonium citrate can be rapidly assimilated by plants, so that conversion into soluble phosphate by means of sulphuric acid is unnecessary.

J. T.

On Sandy Soils and Manuring with Artificial Manures. (*Bied. Centr.*, 1880, 769).—The experiments were instituted on a sandy soil to determine the pecuniary advantage of manuring crops as compared with the value of the unmanured crops. The manures contained phosphates, nitrogen, and potash.

	Average per half-hectare.		
	Value of manure in Marks.	Value of crops in Marks.	+ or - by manuring in Marks.
Potatoes, unmanured	0	93·0	0
„ manured	55·51	211·50	+ 62·99
Oats, unmanured	0	86·68	0
„ manured	36·64	139·78	+ 16·46
Barley, unmanured	0	123·31	0
„ manured	49·37	161·17	- 11·51

E. W. P.

Manuring Potatoes. By J. FITTBOGEN (*Bied. Centr.*, 1880, 712—717).—The manures employed were sodium nitrate at the rate of 50 lbs. per acre, ammonium sulphate at 40 lbs. per acre, kainite at 300 or 400 lbs. of superphosphate 19·5 per cent. at 80 lbs., and a mixture of dried blood, with bone meal containing 6 per cent. of nitrogen and 16 of phosphoric acid at 100 lbs. per acre; mixtures of the above were also used. These manures were put in three weeks before the potatoes were set, excepting the nitrate, which was put on as a top-dressing seven weeks after. The results were as follows: superphosphate alone had no effect as regards yield, but it lowered the amount of dry matter in the tubers; manuring with 200 lbs. of kainite was of little influence, but when 300 lbs. were employed, an increase in yield was the result. Ammonium sulphate was distinctly beneficial both as regards dry matter and yield. The best results were obtained with the mixture of kainite, superphosphate and nitrate of soda, and the second best when ammonium sulphate was substituted for the nitrate. The lowest amount of dry matter was produced in those plots manured with kainite, with or without superphosphate, so that it is evident that this manure lowers the quality of the tubers. Chili saltpetre used as a top dressing has the effect of delaying the ripening, but this is partly counteracted by the addition of superphosphate so as to allow of a larger amount of dry matter to be produced, so the conclusion is drawn that a late top-dressing with this manure is inadvisable. Reckoning up the price of each crop, and setting off against the price the value of the manures employed, it appears that the only crop which brought in a profit was that manured with 300 lbs. kainite; still it must not be considered that kainite is the only manure to be recommended, as a poor soil is much impoverished thereby. With a slightly higher value for the potatoes, ammonium sulphate or kainite with superphosphate produce a slight profit.

The final conclusion drawn is, that the application of nitrogenous and phosphoric manures, without farmyard manure, is much less to be trusted on a poor than on a rich soil.

E. W. P.

Rendering Acid Gases Inactive. (*Dingl. polyt. J.*, 238, 337—344 and 424—428).—This paper describes recent investigations made in reference to former accounts as to the injuries received by plants

from acid gases (*ibid.*, **220**, 87) and to the removal of furnace gases and acid vapours from chemical works.

Schröder has pointed out that the action of sulphurous acid on plants is specially detrimental to their growth, a series of experiments in this direction having proved that hydrochloric and sulphuric acids affect plants in much less a degree than an equivalent quantity of sulphurous acid. Plants which had been exposed to the action of air contaminated with sulphurous acid or hydrochloric acid, showed on examination a considerable increase in the quantities of sulphuric acid and chlorine. Sulphurous acid is absorbed by plants from an atmosphere containing one millionth part of this gas, which becomes oxidised into sulphuric acid.

In order to ascertain the percentage of these gases, it is necessary to use alkalis in incinerating the plants. Different plants absorb different quantities of sulphurous acid during the same time, *e.g.*, oak trees more than fir trees. However, as a rule the differences in the quantities of gas absorbed are not in proportion to the total resistance offered by plants when exposed to long continued action of the gases. Fir trees absorb less acid, but are nevertheless more sensitive than oak trees or any other deciduous tree. Hence they suffer more in an acid atmosphere. The practical examination of the injuries received by plants therefore depends firstly on the externally visible changes which the leaves show, then on the results of the analyses in conjunction with the knowledge of the power possessed by the plants of resisting the action of gases. It is moreover very important not to confound the damage done to the leaves of plants with the appearances originating from fungi, insects, frost, &c.; hence in ascertaining the cause of such injuries, it is absolutely necessary not to choose too late a time in the season, and to consider the normal changes to which leaves are subject every year.

In judging from analytical results, the normal variations often present great difficulties. The amount of sulphuric acid and chlorine present in healthy plants varies considerably, hence the soil, climate, position, and the period of vegetation materially influence the chemical composition.

Schröder in the second part of the paper describes the injurious effects caused by the gases from silver, copper, and lead mines in the Harz Forest. At Clausthal about 10,000 tons of galena are refined annually, at Laubenthal 2,850 tons, and at Altenau 2,200 tons, besides 400 tons of copper pyrites, and 1,000 tons of foreign ores. The whole of the sulphurous acid obtained in the various processes of refining escapes into the air and is equal to 2,500 tons for Clausthal, 650 tons for Laubenthal, and 850 tons for Altenau. As most works are situated in valleys, the acid vapours cannot escape very freely, rising and falling in the direction of the wind. This district has been investigated more closely, and numerous analyses of the leaves and cones of fir trees have been made, confirming Schröder's views with regard to these regions, as it is clearly shown that in the vicinity of the above-named mines vegetation has almost entirely ceased.

Hasenclever has made a series of experiments with a view of ascertaining how much sulphuric acid and chlorine plants can absorb

without being injured. He found that the leaves of several deciduous plants gave as much as 12 per cent. of ash containing one to one and a half per cent. of sulphuric anhydride, and about half a per cent. of chlorine, but was unable to determine the exact limit of absorption.

In conclusion, it is mentioned that the smoke from coal contains large quantities of sulphurous acid and chlorine, and that in manufacturing districts where much coal is consumed, vegetation is greatly retarded. High shafts are only partially effective in preventing the injurious action of acid vapours on plants, as the air does not become sufficiently diluted in wet and sultry weather. Rapid progress is being made in reducing the nuisances arising from chemical works; nevertheless vegetation appears to have ceased to a great extent in the vicinity of such places. At St. Helen's the atmosphere is contaminated every week with the following constituents:—

Gases from fires.....	800	tons sulphurous acid.
Copper works	380	„ „ „
Glass works	180	„ „ „
Chemical works.....	25	„ hydrochloric acid gas.

D. B.

Analytical Chemistry.

Further Remarks on an Iodometric Process. By J. PELLIEUX and E. ALLARY (*Bull. Soc. Chim.* [2], **35**, 10—11).—When using the authors' process (*Bull. Soc. Chim.*, **32**, 273; this Journal, Abstr., 1880) for the determination of iodine in substances, such as kelp-salt, which contain cyanogen and sulphur compounds, the weight of soda-lime employed should be three or four times that of the substance taken for analysis, and the calcination, at a dull red heat, should last for half an hour. If, after the addition of an excess of hydrochloric acid, starch at once gives a blue colour, the calcination has been sufficient, and the subsequent determination will give accurate results. To remove the blue colour thus produced, before proceeding to add the bromate solution, a dilute solution of sodium sulphide should be used, and not sulphurous acid or an alkaline thiosulphate. Allowance must be made for the action of any excess of sulphide on the bromate solution. The yellow colour sometimes caused by the presence of small quantities of iron does not interfere with the determination of the end-point of the reaction. C. H. B.

Oxygen Absorption of Alkaline Pyrogallate. By T. WEYL and X. ZEITLER (*Annalen*, **205**, 255—264).—The authors have investigated the relation of the amount of absorption to the quantity of pyrogallol and the concentration of the alkaline solution. The principle of the method used consists in passing a given volume of air through alkaline pyrogallate and titrating the unabsorbed oxygen by

sodium hydrosulphite (Schützenberger's method). Some of the results are tabulated below, 750 c.c. of moist air being used in each determination:—

Temp.	Bar.	Volume of dry oxygen corresponding to 750 c.c. moist air.	Volume of dry oxygen unabsorbed.	
			c.c.	Per cent.

0.25 gram Pyrogallol in 10 c.c. KHO of 1.025 sp. gr.

15°	741.8 mm.	143.6	2.49	1.73
19	735.6	139.0	2.16	1.57

0.25 gram Pyrogallol in 10 c.c. KHO of 1.05 sp. gr.

19°	733.7 mm.	138.6	1.19	0.88
15	741.8	143.6	1.26	0.88

0.25 gram Pyrogallol in 10 c.c. KHO of 1.5 sp. gr.

18°	734.6 mm.	139.6	4.05	2.9
1	735.3	140.3	5.08	3.6

From the results it appears that the absorptive form of alkaline pyrogallate is a function of the alkalinity of the solution. V. H. V.

Estimation of Small Quantities of Carbon Bisulphide. By A. W. HOFMANN (*Ber.*, 13, 1732—1737).—The method described depends on the formation of the red compound, PET_3CS_2 , with triethylphosphine; for this purpose the substance containing the carbon bisulphide is placed in a retort connected with a receiver, and with two or three test-tubes which contain some triethylphosphine floating on caustic soda. The retort is heated on a water-bath, and a current of dry carbonic anhydride passed through the whole apparatus; in this manner all the carbon bisulphide present is brought in contact with the triethylphosphine, and the above-mentioned compound is formed. At the end of the experiment, the red compound is collected on a weighed filter, dried in a vacuum, and weighed. By this means the author has been able to estimate the amount of carbon bisulphide which occurs in mustard oil from *Sinapis juncea*, *Sinapis nigra*, and also in artificial mustard oil, all varieties containing small quantities.

P. P. B.

Estimation of Carbon Bisulphide. By J. MACAGNO (*Gazzetta*, 10, 485—489).—The extensive use of carbon bisulphide as a remedy for phylloxera rendered it necessary to estimate the diffusion of the vapour in the soil, and for this purpose the author has applied the

xanthic acid reaction. The liquid containing the carbon bisulphide is added to an alcoholic solution of potash, or the air from the soil is passed through it, when the bisulphide unites with the potassium ethylate to form potassium xanthate; the amount of the latter is then estimated as cupric xanthate by adding a decinormal solution of cupric sulphate (12.47 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per litre) until there is a slight excess of the copper salt. This is easily ascertained by placing a drop of the liquid from time to time on a white porcelain plate in the usual way and testing with potassium ferrocyanide. Each c.c. of the copper solution corresponds with 0.0076 gram carbon bisulphide. The analysis is easily and quickly made, and may be used to detect adulteration of commercial bisulphide. C. E. G.

Chemical Toxicology of Phosphorus. By F. SELMI (*Gazzetta*, 10, 437—442).—The author first criticises the processes proposed by Scherer and by Mitscherlich for the detection of phosphorus in the free state. In the former, even when hydrogen sulphide is absent, the paper moistened with silver nitrate is occasionally blackened by the action of volatile reducing agents; to avoid this difficulty, paper and silver nitrate, absolutely free from phosphoric acid, must be used, and fresh pieces of paper are employed successively until they cease to be blackened; the papers are then incinerated and the residue tested for phosphoric acid. Instead of Mitscherlich's process, it is proposed to distil the suspected substance with water in a current of carbonic anhydride, agitate the aqueous distillate with carbon bisulphide to take up the phosphorus, add a little absolute alcohol to the separated bisulphide, and allow the latter to evaporate. In this way an alcoholic solution of phosphorus is obtained which is divided into two portions, to one of which is added an alcoholic solution of mercuric iodide, and to the other silver nitrate; if phosphorus is present, a yellow coloration will be produced by the former, and a brown by the latter with subsequent deposition of brown flocks. The green coloration which phosphorus gives to the hydrogen flame may also be employed in testing the alcoholic solution.

It is stated that in cases of poisoning with phosphorus it is useless to examine the urine; this, however, is incorrect. Tested by the modification of Scherer's method above described, phosphorus can be detected. If the urine is rendered alkaline with baryta-water and then precipitated by adding absolute alcohol, the precipitate gives the reactions of the lower acids of phosphorus with nascent hydrogen. On distilling the alcoholic filtrate, a volatile neutral principle passes over containing phosphorus and also a phosphorus base.

An examination of the brain and liver of a subject poisoned with phosphorus gave similar results: the lower acids of phosphorus could be detected, as well as neutral and basic phosphorus compounds similar to those found in the urine. C. E. G.

Determination of the Relative Values of Precipitated and Soluble Phosphates. By A. EMMERLING (*Bied. Centr.*, 1880, 718—724).—Generally superphosphates are to be preferred to precipitated phosphates, and the ratio of their effects on crops is as 2 : 1. On clay

lands, precipitated phosphates must be added in quantities equal to twice that of the superphosphate; on humous sandy soils, superphosphate is also better, but on marshy lands, where there is already a considerable supply of phosphoric acid, good results are not obtained. On moorland, precipitated calcium phosphate, however, appears to be better than superphosphate, and both, when in conjunction with kainite, yield like results. The experiments were made in Holstein on cereals.

E. W. P.

Use of Sodium Hyposulphite (Na_2SO_3) in the Estimation of Copper, of Indigo, and of Dissolved Oxygen in Water. By A. BERNTHSEN (*Ber.*, 13, 2277—2283).—Since sodium hyposulphite, prepared by the action of metallic zinc on an aqueous solution of sodium hydrogen sulphite, contains considerable quantities of sodium sulphite and thiosulphate, Goppelsröder's proposal (*Bull. soc. ind. de Mulhouse*, 1873, 643) to determine the strength of the solution by titration with permanganate is not trustworthy. Accurate results are, however, obtained by a modification of the process recommended by Tiemann and Preusse (*Ber.*, 12, 1778; this Journal, 1880, Abstr., 137). The operation is conducted in a three-necked Woulf's bottle, the centre tubulus of which is fitted with a double-bored cork containing two drawn-out pieces of glass tubing, which are attached by short pieces of caoutchouc to two burettes containing respectively the sodium hyposulphite and the indigo solutions. The open end of the burette for the hyposulphite is provided with a U-tube containing pieces of pumice which have been saturated with ferrous sulphate and dipped in a solution of soda.

A standard copper solution is prepared by adding excess of ammonia to an aqueous solution of 4.5346 grams of crystallised copper sulphate and diluting to a litre with water free from air. The standard indigo is made by dissolving 50 grams of commercial indigotin (sodium indigo sulphate) in a litre of water and diluting until its strength is equal to that of the standard copper. Having brought 15 or 25 c.c. of the copper solution into the apparatus the air is expelled by a current of hydrogen which enters at the first tubulus (having previously passed through a U-tube containing ferrous hydrate and pumice-stone) and escapes at the third neck of the flask through a bent tube, the end of which dips under water. The hyposulphite solution is slowly added until the blue colour of the copper is nearly destroyed. One or two drops of indigo are next added, and the hyposulphite is carefully dropped in until the mixture is colourless.

Each c.c. of copper solution corresponds to 1 mgm. Na_2SO_3 .

W. C. W.

Titration of Hyposulphite with Indigocarmine. Quantitative Estimation of Indigo. By A. BERNTHSEN and A. DREWS (*Ber.*, 13, 2283—2285).—The solution of sodium hyposulphite may be standardised by titration with a dilute solution of indigotin instead of ammoniacal copper sulphate. If the indigo solution is prepared from commercial indigotin its strength must be ascertained by titration with sodium hyposulphite. A solution, 2 c.c. of which corresponds

to 1 mgm. Na_2SO_3 can be prepared by dissolving 1.191 grams of pure indigotin in the smallest amount of sulphuric acid requisite, neutralising with sodium carbonate and diluting to a litre.

Attempts to estimate commercial samples of indigo by titration with sodium hyposulphite did not yield satisfactory results.

W. C. W.

Chemical Toxicology of Arsenic. By F. SELMI (*Gazzetta*, 10, 431—437).—The author points out that the great difficulty in toxicological research is to obtain reagents in quantity of absolute purity, and this is especially the case in testing for arsenic. The best method of purifying the zinc from the traces of arsenic it almost invariably contains is to melt it in a crucible and then plunge into it a piece of sal-ammoniac, pressing it firmly against the bottom of the crucible; a lively ebullition takes place and the arsenic is removed as chloride; if it still contains a minute trace of arsenic, a second operation will entirely remove it. It should give no signs of blackening in Marsh's apparatus even after the gas has passed for an hour. The author finds that the method generally recommended for purifying sulphuric acid from arsenic, namely, to add some oxidising agent and distil, is not effective, as traces of arsenic acid pass over with the sulphuric acid. He recommends to add 10 to 15 per cent. of lead chloride to the sulphuric acid and heat gradually; the chloride slowly dissolves with evolution of hydrochloric acid, which carries off the arsenic as chloride; the acid is then distilled and the first portions rejected; as soon as the distillate is found to be free from every trace of arsenic it is collected for use.

The best method of removing the organic matter is to treat the substance by Gautier's method until most of the organic matter is destroyed, decompose the nitrous products with sulphurous anhydride, and after mixing the residue with sulphuric acid to heat it in an oil-bath at 130° in a current of hydrochloric acid gas, which carries off the arsenic as trichloride. The gas issuing from the apparatus is absorbed by distilled water.

A special arrangement of Marsh's apparatus is described in which one portion of the tube, about 25—28 cm. long, is kept red-hot and the other cold, the current of hydrogen being passed slowly; in this way $\frac{1}{400}$ mgm. of arsenic may be detected.

The author notices that arsenious anhydride is volatile to a very slight extent at 100° , and considerably more so at 130° ; also that when acid solutions containing arsenic are agitated with ether the latter takes up traces of arsenic.

The author is undertaking experiments to ascertain in what state arsenic occurs in the urine of subjects poisoned with arsenic. Arsenic was administered to a large dog in doses too small to produce fatal effects, and the urine examined over a considerable period. It was found that during the first period of three days the urine contained an acid of arsenic precipitable by baryta, and another arsenical compound which was not precipitated by baryta; the same substances were found in the second period of five days, besides a volatile arsenical compound which gave a crystalline hydrochloride; subsequent to this, the arsenical base gradually disappeared.

C. E. G.

Estimation of Nitrogen Compounds in Plants. By E. SCHULZE and J. BARBIERI (*Landw. Versuchs.-Stat.*, **26**, 213—283).—Recognising the necessity of a reformation in the methods of analysis as applied to the estimation of the nitrogenous constituents of vegetables, the authors have endeavoured, by means of a combination of the results already arrived at by others, or in the course of their own researches, to offer a critical account of the best methods obtainable for a solution of the difficulty. The lack of accurate qualitative knowledge of the various forms in which nitrogen exists in plants is a difficulty which must be overcome before a good system of analysis can be framed; in the present state of our knowledge, only certain general lines of procedure can be indicated, having for their aim the division of nitrogenous bodies broadly into groups, such as albuminoid, peptoid, amido-compounds, and the like. It is of the first importance therefore in the analysis of vegetable substances that in the extraction of the nitrogenous constituents the latter should undergo little or no change in composition; this may be best effected according to the authors by extraction first with cold and then with hot water, the cold water dissolving out any acid present which would when heated decompose some of the amido-compounds with formation of ammonium salts. Extraction with dilute alcohol, according to Kellner's method, is also recommended. For the estimation of ammonia originally present in the plant, Emmerling's method, consisting of treatment with milk of lime in the cold under reduced pressure, is noticed as giving reliable results.

Of primary importance, however, are the methods for the estimation of albumin, of which several have been proposed by Ritt-hausen, Hofmeister, Kellner, and others, based on precipitation by such reagents as the hydrates or acetates of lead, copper, or iron. After remarking on the various merits of these proposals, and showing that it is in most cases best to estimate the albumin by difference, the authors confess that it is uncertain whether by the use of the above reagents other non-albuminoid bodies are not simultaneously precipitated: it is therefore necessary to make more than one albuminoid precipitation, and to use various precipitants, such as tannin, ferric acetate, &c., in order by a comparison of the numbers obtained to arrive at a true result; for if one precipitant is found to throw down less nitrogen than another, the filtrates in both cases being free from albumin, the lower number will represent the more accurate result. As a test for the presence of albumin, the reaction with ferrocyanide of potassium and acetic acid is recommended. In nutritive value the peptones approach very near, if they do not equal, albuminoids; after the separation of the latter, they may be precipitated by means of phosphotungstic acid. When this reagent was used in the case of extract from the sprouts of young lupines, it was found that a large quantity of other substances was precipitated along with peptone; these are not thrown down by tannin, like ordinary peptone, but consist apparently of decomposition-products of albumin, holding a position intermediate between peptone and the crystalline final decomposition-products of albumin. Where then it is required to ascertain the amount of peptone alone, the phosphotungstic acid

should be added until the filtrate no longer gives the peptone reaction with sodium hydrate and copper sulphate.

For the estimation of asparagine and glutamine, Sachsse's method is very convenient; it consists in converting these bodies into ammonium salts by boiling with an acid, and then determining the ammonia by means of sodium hypobromite; this reagent, however, liberates nitrogen from other organic bodies, namely, leucine, creatine, caffeine, and others. The results of this method are therefore not always reliable, although in the case of young lupines it was found that the amount of asparagine calculated from analysis agreed very nearly with the quantity obtained by crystallisation. Amido-compounds in general are estimated with more certainty by the method of Sachsse and Kormann, in which the acid amides are first decomposed by boiling with dilute acid into amido-acids, and the latter, after the removal of ammonia salts, treated with potassium nitrite and dilute sulphuric acid, the evolved nitrogen being accurately measured. By this means all known amido-compounds are decomposed, and the results therefore in all probability cannot be too low. Absence of albumin and peptones must of course be ensured before an estimation of the amido-compounds can be made. That the latter bodies do not represent the whole of the nitrogen still left in vegetable extract after the removal of albuminoids and peptones is seen from the following analytical results:—

	A. Nitrogen in extract after precipitation with phospho- tungstic acid.	B. Nitrogen in the amido-form.	Difference.
	Per cent.	Per cent.	Per cent.
6 days old lupines	3·32	2·85	0·74
12 " " "	6·01	5·59	0·42
15 " Soja sprouts	3·00	2·47	0·53
15 " marrow sprouts	3·28	2·44	0·84
Birch leaves	1·06	0·66	0·40
Young grass	0·46	0·22	0·20

The above numbers lead to the conclusion that in the extracts under investigation nitrogen-compounds were present which were left either wholly or partially unaffected by the action of nitrous acid.

In conclusion, the authors suggest that in all analyses of vegetable extracts the nitrogen estimation should be so carried out as to allow of the division of the nitrogen into three distinct groups, namely, (1) albuminoid, (2) non-albuminoid, but thrown down by phosphotungstic acid, and (3) nitrogen in the filtrate from the phosphotungstic acid precipitate. The following analyses may serve as examples of the application of this method.

	Total nitrogen.	Albuminoïd nitrogen.	Non-albu- minoïd pre- cipitated by phospho- tungstic acid.	Nitrogen in filtrate from latter.
Lupine seeds.....	8·63	8·17	0·24	0·22
Soja beans.....	6·73	6·32	0·13	0·28
11—12 days old sprouts of lupines	10·64	3·40	1·60	5·64
12 days old ditto	10·51	2·33	2·17	6·01
15 days old sprouts of Soja beans	7·42	3·86	0·56	3·00
Birch leaves	4·32	3·11	0·15	1·06
Young grass	2·22	1·55	0·21	0·46

J. K. C.

Detection of Alcohol in Transparent Soaps. By H. JAY (*Bull. Soc. Chim.* [2], **35**, 51—52).—Introduce 50 grams of the finely divided soap into a flask of about 200 c.c. capacity, mix with 30 c.c. strong sulphuric acid, and agitate until solution is complete. Fill up the flask with water, allow the fatty acids to settle and solidify, withdraw the supernatant liquid, nearly neutralise, and distil. Test the first 25 c.c. of the distillate for alcohol by the method of Riche and Bardy;—add 0·5 c.c. sulphuric acid of 18° B., then 0·5 c.c. potassium permanganate solution, containing 15 grams per litre; allow to stand *one minute*, then add eight drops sodium thiosulphate solution of 33° B., and 1 c.c. of a solution of magenta containing 0·1 gram per litre. If alcohol is present, a distinct violet coloration will be produced in about five minutes; if the coloration does not appear after fifteen minutes, it may be concluded that alcohol is absent. The presence of essences in the distillate does not interfere with the conversion of the alcohol into aldehyde.

C. H. B.

Testing for Sulphuric Acid in Wine and in Vinegar. By A. CASALI (*Gazzetta*, **10**, 475—478).—After pointing out the defects in the processes employed for detecting free sulphuric acid in wine or vinegar the author describes a new method, which is simple and of great delicacy. The liquid is ground up in a mortar with finely powdered porcelain (about 4 parts), so that the mixture is not moist to the touch. The porcelain powder must be treated previously with hydrochloric acid to remove every trace of free alkali. The mixture is then ground up with ether, thrown on a filter, and washed with ether (using about 4 parts in all), a little water is added to the colourless filtrate, and the ether distilled off. In this way the sulphuric acid is left in the aqueous solution, and may readily be detected by the usual tests. The ether employed should be freed from every trace of acid by agitation with magnesia and water. By this process 0·001 gram sulphuric acid in 10 c.c. wine can readily be detected.

C. E. G.

Detection of Rosaniline in Wine. By F. KÖNIG (*Ber.*, **13**, 2263—2264).—Adulteration of wine with rosaniline can be detected

by boiling about half a gram of white woollen thread in 50 c.c. of the wine to which sufficient ammonia has been added to change its colour to a dirty green. After the excess of ammonia has been expelled by boiling, the wool is washed with water, and pressed and moistened with a solution of potash. On heating the wool in a test-tube it dissolves, forming a brown liquid, which is mixed with half its volume of pure alcohol, and extracted with ether. On the addition of a few drops of acetic acid to the ethereal solution a red coloration will be produced if the wine contains even a trace of rosaniline.

W. C. W.

Optical Estimation of Cinchonidine in Commercial Quinine Sulphate. By O. HESSE (*Annalen*, **205**, 217—222).—The only alkaloids present in the cinchona barks which have any influence on the quality of the quinine are cinchonidine and homocinchonidine. But in the method of manufacture, the homocinchonidine is so far separated by crystallisation that quinine sulphate does not contain more than 1 per cent. of homocinchonidine sulphate. On the other hand, quinine sulphate always contains a considerable admixture of cinchonidine sulphate, which is neglected by the ordinary proof-tests of commercial preparations. The author proposes to estimate the amount of impurity of cinchonidine sulphate by the optical rotatory power of a solution ($2 : 10\text{HCl} : 15\text{H}_2\text{O}$) of the sample of the sulphate ($l = 220 \text{ mm.}$, $t = 15^\circ \text{C.}$). The principle of the calculation is as follows:—if α be the angle of rotation of dry anhydrous quinine sulphate, β the angle of anhydrous cinchonidine sulphate, γ the angle of the mixture, then if x be the quantity of quinine and y the quantity of cinchonine sulphate, then the relative percentage of cinchonidine sulphate is expressed by the formula $y = \frac{\alpha - \gamma}{\alpha - \beta}$. Or again, if a, b , and

be the specific rotatory powers of quinine, cinchonidine, and the mixed sulphates, then the relative proportion of cinchonidine sulphate is expressed by the formula $y = \frac{a - c}{a - b}$. For α and β the author has found the numbers -40.309° and -26.598° , hence the first formula becomes $y = \frac{40.309 - \gamma}{13.711}$, and the second $y = \frac{229.03 - c}{77.9}$.

Experiments are quoted to show the agreement of values obtained by experiment with those calculated from these formulæ. This method is, however, only applicable for mixtures of quinine and cinchonidine sulphate; but the small quantity of homocinchonidine present in commercial samples will not materially interfere with the results obtained. As, however, cinchonidine sulphate does not exist in quinine sulphate as anhydrous but as a hydrated (5 mols. H_2O) salt, the author modifies the formulæ above. The first becomes $y = (40.309 - \gamma)8.250$, and the second $y = (229.03 - c)1.452$.

V. H. V.

Estimation of Glucose in Urine. By G. CARNELUTTI and L. VALENTE (*Gazzetta*, **10**, 473—475).—As more or less of the cuprous oxide which is formed when diabetic urine is treated with Fehling's test remains in solution, giving a red colour to the liquid, the estimation of

the glucose is vitiated. The author has endeavoured to remedy this by removing the substance which keeps the cuprous oxide in solution, before adding Fehling's test. For this purpose, a measured volume of the urine (100—200 c.c.) is evaporated to a syrup on the water-bath, 1 c.c. of a 25 per cent. solution of zinc chloride previously mixed with one-fourth its volume of hydrochloric acid is added, then 2 vols. of absolute alcohol, and the whole left to stand for some hours. It is then filtered, the residue washed with alcohol, and the solution after removal of the alcohol by evaporation, made up to the original volume with distilled water, the glucose being determined in this in the usual way. By this method, excellent results were obtained not only with urine to which glucose had been added, but also with diabetic urines.

C. E. G.

Urea, Sugar, and Sodium Hypobromite. By G. ESBACH (*Bull. Soc. Chim.* [2], **34**, 632).—A solution of pure glucose, whether boiling or not, evolves a small quantity of gas when treated with sodium hypobromite; cane-sugar yields no gas. In aqueous solutions of urea, the excess of gas above the 92 per cent. which urea yields under normal conditions, varies with the quantity of sugar added, with the nature of the sugar, the strength of the urea solution, and the composition, especially the alkalinity of the hypobromite. Urea added to a true diabetic urine evolves only 92 per cent. of its nitrogen. For small quantities of glucose, such as those present in diabetic urine, the excess of gas given off is sensibly proportional to the mass of the sugar, but this does not hold good for large quantities. Jay has shown that the same is true for cane-sugar. It follows that sugar should not be added to urine before estimating the amount of urea by means of hypobromite. The presence of glucose in diabetic urine causes the urea in such urine to give off the whole of its nitrogen, but the error produced is rarely as high as 1 per cent., and is quite negligible in practice, especially if the hypobromite used does not contain a large excess of soda.

C. H. B.

Wax and Honey. (*Dingl. polyt. J.*, **238**, 356.)—Hager mentions that white wax contains 3 to 5 per cent. of tallow, and that manufacturers add turpentine or resin in order to impart to wax the requisite tenacity. Hence these additions, unless present in large quantities, cannot be regarded as adulterants.

The sp. gr. of wax when higher than 0.964 indicates the presence of stearin, resin, or Japan wax, and when lower than 0.956 paraffin, ozokerite, or tallow are present. Chloroform or fatty oils form a clear solution with dry wax and a slightly turbid solution with moist wax. By treating pure beeswax with a saturated solution of borax at 80°, the aqueous solution is rendered turbid; when Japan wax or stearin are present, a milky solution is obtained, remaining opaque after cooling. By boiling wax in a solution of soda (1 : 6) pure wax gives a translucent solution, if milky, stearin is present, if pasty or stiff, Japan wax has been added. When the sp. gr. is less than 0.956, and the wax behaves with borax and soda like pure wax, paraffin or ozokerite has been added; the same result is obtained when the sp.

gr. is correct and the borax or soda test indicates the presence of Japan wax.

Ceresin (yellow or white) forms milky solutions in the borax or soda test, or behaves like beeswax, but has a lower sp. gr. With regard to the adulteration of honey with the artificially prepared product (adulterated with large quantities of starch-sugar) Planta-Reichenau proposes to estimate the amount of grape-sugar before and after inversion with a 2 per cent. solution of sulphuric acid. Pure bees' honey yields about 8 per cent. grape-sugar, whilst honey adulterated with starch-sugar shows as much as 45 per cent.; moreover, pure honey contains 63—71 per cent. of grape-sugar already formed; artificial honey only 29—37 per cent. D. B.

Presence of Corn-cockle Seeds in Meals. By A. PETERMANN (*Bied. Centr.*, 1880, 748—752).—The seeds of several weeds, such as those of *Sinapis arvensis*, *Melampyrum arvense*, &c., occur in meals, but the most objectionable and dangerous are those of the corn-cockle. It imparts to the bread made from the meal a bitter taste, and acts prejudicially on the persons who partake of such bread. The amount of this seed in cereals is sometimes large; for example, in a sample of rye, as many as 927 seeds per kilo. were found. If the meal is passed through a sieve having meshes 1 mm. broad, the husks will remain in the sieve, and are to be recognised by their dark colour. On treatment with a solution of calcium chloride (1 : 3) or glycerol, characteristic appearances of the various seeds are observable (for these appearances *vide Bull. Acad. Belg.*, 1879). The starch grains of the corn-cockle present no remarkable appearances whereby they can be easily recognised. They are very small, measuring 0.006 mm. To detect them, 500 grams must be digested with a litre of 85 per cent. alcohol, and filtered while hot. The filtrate is precipitated by absolute alcohol, and the precipitate dried, and then taken up with cold water. This extract is again precipitated by alcohol, the precipitate dried, and, if of a yellowish-white colour, of a bitter, burning taste and soluble in water, it consists of saponin derived from the corn-cockle. E. W. P.

Technical Chemistry.

New Developers for Silver Bromide Dry Plates. By J. M. EDER (*Dingl. polyt. J.*, **238**, 57—59).—The author speaks favourably of Abney's "Hydroquinone Developer" (*Photographic News*, 1880, **24**, 346), but condemns various iron salts proposed by Cary Lea (*Brit. Jour. Phot.*, 1880, **27**, 280 and 292).

Edward's Glycerine-Pyrogallic Developer (*Photographic News*, 1880, **24**, 177) is warmly recommended.

Henderson's Ferrocyanide Developer (*Brit. Jour. Phot.*, 1879, **26**, 36) is said to give variable results.

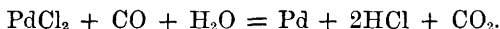
J. T.

Carbonic Oxide in the Air of Rooms. (*Dingl. polyt. J.*, **237**, 455—459).—C. H. Wolff describes a small apparatus for drawing air through powdered glass moistened with diluted blood; 3 parts carbonic oxide in 10,000 can be clearly detected after washing out the blood and agitating with a drop of ammonium sulphide, after which the bands can be easily seen in the spectroscope.

Jägerholm takes equal parts of defibrinated blood and cold saturated borax solution to prepare a blood solution, which retains its properties for some time. Such a preparation containing carbonic oxide shows the reaction after being kept for three months.

If 10 c.c. of blood be shaken five to seven times, and each time with 6 litres of air containing 0.5 part carbonic oxide per 10,000, on warming the blood to 90—95° and passing air through it which subsequently passes through a neutral solution of 1 part palladium chloride in 500 parts water, the palladium is precipitated. In this way carbonic oxide can be detected in the blood of dogs which have breathed for some time an atmosphere containing 0.4 part in 10,000.

Foder proposes a qualitative test by means of strips of fine filter paper soaked in a solution of 0.2 gram palladium chloride in 100 c.c. water. The dried slip is placed on platinum wire in a 10-litre flask with a few c.c. of water, and the flask is corked. With 5 parts of carbonic oxide a black glistening skin forms on the paper in a few minutes, with 1 part after 2 to 4 hours, and with 0.5 part after 12 to 24 hours. For quantitative estimation, a considerable volume of air can be drawn through a neutral palladium chloride solution, and the amount of the precipitated palladium determined; the decomposition is as follows:—



53.24 palladium corresponds to 14 carbonic oxide.

By this process carbonic oxide has been detected in three bodies which had been buried over two months. As this blood was dry no carbonic oxide could be detected by the spectroscope in an aqueous solution. J. T.

Incineration of Seaweeds in the Manufacture of Iodine. By THIERCELIN (*Bull. Soc. Chim.*, **33**, 559—563).—Most seaweeds contain iodine, but the richest in that element is the *Fucus digitatus*, and this contains more iodine in winter than in summer. Instead of partially drying it and then incinerating in pits, as is the usual practice, the seaweed fresh from the coast is burnt in a specially constructed furnace, like a long reverberatory furnace, communicating with an arched flue 5 metres long, the floor of the whole being on an incline of 12°: immediately above the furnace is an evaporating pan to evaporate the solutions. In working, the hot air from the furnace dries the seaweed in the flue, through openings in the side of which it is gradually pushed downwards towards the fire. As the seaweed is consumed, fresh quantities are introduced through an opening at the upper end of the flue, which is kept closed at other times. The seaweed is also spread over the top of the flue, and is there partially dried. Any reserve of the seaweed is put into

large tanks, where it enters into fermentation, at first alcoholic, but afterwards putrid. Attempts to collect the alcohol formed were unsuccessful. After the fermentation has continued five or six days the plants are pressed, the pressed cakes are burnt in the furnace, and the expressed liquid first evaporated in the evaporator, and then burnt. The advantages of this method are that it is independent of the weather, the plant itself furnishing the fuel to dry it; the ash is uniform and well burnt, and the yield of iodine is large, about 0.5 per cent. in summer, and 1.4 to 1.5 in winter.

C. E. G.

Extraction of Potassium Iodide from Kelp. By E. ALLARY and J. PELLIEUX (*Bull. Soc. Chim.* [2], **34**, 627—630).—The mother-liquors from which the chlorides and sulphates have been separated are evaporated to dryness in a furnace of special construction, and the residue is carefully roasted, until all the sulphur is either expelled or oxidised. No iodine is lost in this operation. It is necessary to stop the roasting as soon as the sulphur compounds are completely oxidised; this may be ascertained by withdrawing samples from time to time. The calcined mass is broken up and subjected to methodical lixiviation with cold water, in a small Shænk's apparatus. The solution, when evaporated to dryness, gives a white salt, which contains about 50 per cent. of iodides. This salt is powdered, and introduced into a Dorevaut's digester, which may be used either as an extractor or as a still. In this it is treated with warm alcohol, which dissolves out the iodides. When the extraction is complete, the alcohol is distilled off in the same apparatus, and used again. The salt thus obtained is a mixture of potassium and sodium iodides, containing on an average 34 per cent. of the former and 66 per cent. of the latter. To convert the sodium iodide into the potassium salt, its amount is determined, and to the saturated aqueous solution of the mixed salts is added a saturated solution of potassium carbonate, containing an amount equivalent to the sodium iodide present, and a stream of cooled carbonic anhydride from the furnaces is passed into the mixture. The following reactions take place:—(1) $2\text{NaI} + \text{K}_2\text{CO}_3 = 2\text{KI} + \text{Na}_2\text{CO}_3$; (2) $\text{KI} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = \text{KI} + 2\text{NaHCO}_3$. When the conversion of the sodium carbonate into bicarbonate is complete, the crystals of the latter are removed, and the small quantity of bicarbonate remaining in solution is exactly decomposed by means of hydrochloric acid. The solution then contains potassium iodide, mixed with a small quantity of sodium chloride, which may be separated by repeated crystallisation. All the residues are worked up in the treatment of fresh quantities of kelp, and thus loss of iodine is avoided.

To prepare pure potassium iodide, the salt obtained by the above method is treated with alcohol, and the dissolved iodide recrystallised.

C. H. B.

Analyses of Marine Algæ. By E. ALLARY (*Bull. Soc. Chim.* [2], **35**, 11—12).—The following analyses were made on the fresh algæ collected on the shores of Brittany:—

Species.	Kilos. varec per 1,000 kilos. of ash.	Kilos. soluble matter per 1,000 kilos. of ash.	Kilos. iodine per 1,000 kilos. of varec.	Kilos. iodine per 1,000 kilos. of soda.
<i>Digitatus stenolobus</i> —				
New leaf	18,752	582	1·224	22·952
Foot	16,988	527	1·089	18·500
Old leaf	16,166	502	0·578	9·344
Whole plant	20,095	765	0·606	12·177
<i>Digitatus stenophyllus</i>	20,255	714	0·996	20·174
<i>Saccharinus</i>	18,906	711	0·448	8·470
<i>Alaria</i>	21,080	700	0·108	2·277
<i>Vesiculosus</i>				
<i>Nodosus</i>				
<i>Serratus</i>				
<i>Siliquosus</i>				
} black-wrack (mean) ..				
<i>Loreus</i>	16,401	720	0·087	1·443
<i>Bulbosus</i>	21,565	738	0·077	1·660

The percentage amount of iodine varies greatly in different species, and for the same species varies with the latitude.

Digitatus stenolobus grows in a peculiar manner. At the base of each leaf there forms; at a certain period, a new leaf, which gradually pushes the old one before it, until the latter withers, and in the month of April falls off. From the above table it will be seen that the iodine exists in the different parts of the plant in the following ratios:—

New leaf	100·00
Foot or stalk	88·97
Old leaf	47·22

It is evident that when the leaf ceases to grow and loses its vitality, it gives up a portion of its iodine to the surrounding water.

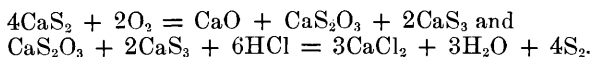
C. H. B.

Extraction of Phosphoric Acid. By A. COLSON (*Bull. Soc. Chim.*, **33**, 563—564).—This process consists in treating the natural phosphate in lumps with dilute hydrochloric acid in wooden vats, and allowing to stand 24 hours. The clear solution is separated from the insoluble portion, which is washed, the washings serving instead of water to dilute fresh acid. The clear liquid is then mixed with the proper proportion of sulphuric acid, of 50° B., the calcium sulphate separated by pressure, and the solution, containing hydrochloric and phosphoric acids, is concentrated, the hydrochloric acid being collected in an ordinary condensing column. In this way a solution containing 400—500 grams P_2O_5 , and 40—100 grams HCl per litre is obtained. The method would appear to be peculiarly applicable to phosphates containing alumina and iron, in which there is a great loss of phosphoric acid when treated directly with sulphuric acid in the ordinary way. Excess of hydrochloric acid must not be used in treating the crude phosphate.

C. E. G.

Novelties in the Soda Industry. (*Dingl. polyt. J.*, **239**, 47—56).—For the recovery of sulphur by the decomposition of sulphuretted alkaline earths, Aarland proposes to use chloride of calcium instead of chloride of magnesium (recommended by Schaffner and Helbig), as according to his views it is difficult to work up magnesia liquors.

Pechiney subjects the yellow liquors obtained from soda-residues to the action of the atmosphere, until the whole of the sulphur is precipitated, when neutralised with an acid. The following reactions are said to take place:—



Dalhousie Ross recommends the use of superheated steam in recovering sulphur from sulphuretted residues.

Briegleb has patented an arrangement for the uniform distribution of liquids specially applicable to Gay-Lussac or Glover towers. Nobel's specification describes an apparatus used for concentrating sulphuric acid, the particulars of which cannot be understood without the drawing which accompanies the original paper.

Hartman proposes to concentrate sulphuric acid from the chambers in iron vessels; however, to avoid the destructive action of the acid on the iron, he adds sulphate of iron, which after concentration again crystallises out.

Jürisch gives some analyses of a series of samples of raw soda made at Muspratt's works, which appear to confirm the fact that almost all impurities in raw soda liquors are transferred to the red liquors in the balling process; further, that in oxidising the latter the "sulphate of sodium" is converted into the thiosulphate, and that in causticizing, according to Parnell, the latter is partly reconverted into sulphide and sulphite of sodium. At this stage of the process, the lime simultaneously precipitates silicic acid, alumina, and ferric oxide, and apparently also small quantities of cyanogen.

In a second series of experiments the results showed that the quantity of cyanogen compounds depends solely on the amount of undecomposed "sulphate" present, no matter whether present during the entire melting process, or only at the end of the same.

The preference given to the Pechiney-Weldon process is due to the fact that a product is obtained, which almost invariably contains the same known quantities of undecomposed "sulphate," sufficient to reduce the amount of cyanides to the same level as the quantity present in "hand-furnace liquors." If the contents of the revolver be emptied sooner than is usual, the resulting raw soda would in some cases be lixiviated readily, in others with difficulty, and would contain either much cyanogen or undecomposed "sulphate," or very little of either.

Thelen has altered his evaporating and drying apparatus, frequently quoted, in a manner which enables him to use it with advantage for roasting ores. A description of his modification would, however, be imperfect without the accompanying drawing.

In order to desulphurise soda-liquors according to Parnell, the crude liquor is treated with metallic zinc; Scheurer-Kestner, however, uses

zinc hydrate, prepared from chloride of zinc by precipitation with lime, until a portion of the filtrate examined is free from sulphur. The desulphurised liquor is syphoned off after settling, the resulting sulphide of zinc washed and treated with hydrochloric acid. The solution of chloride of zinc is again precipitated with lime, and used for desulphurising a further quantity of soda-liquors.

The soda-liquors and acids containing metals such as arsenic, &c., are purified at the works belonging to Merle and Co., by passing an electric current through the same. Wastchuck and Glouchoff intend to carry on the whole operation of alkali-making by electrolysis, and have patented a process, which is described and illustrated more minutely in the original paper.

Unger has materially improved his well-known apparatus for the preparation of soda by means of ammonia and carbonic acid, which facilitates the operation very considerably. D. B.

Technical Notes. By G. LUNGE (*Dingl. polyt. J.*, **238**, 69—77).—*Decomposition of Sodium Sulphate by Lime.*—The influence of various pressures, temperatures, and admixtures of water and lime has been examined. Sealed glass tubes were employed, and the pressure was roughly estimated from the temperature. Only in one case was a pressure above 5 atmospheres obtained. The best result was obtained at a temperature of 150—175°, pressure 5—8.5 atmospheres; 1 part sulphate, 1 part lime, and 25 parts water gave 31.7 per cent. of the sulphate converted into hydrate. The decomposition is so imperfect that the process cannot be applied practically.

Decomposition of Sodium Sulphate by means of Barium Carbonate and Caustic Lime.—Hill found that sodium sulphate boiled with an equivalent each of barium carbonate and lime under pressure, the sulphate was converted completely into caustic soda. Wartha has shown that the decomposition goes on in open vessels. Wartha's results were confirmed. Both freshly precipitated barium carbonate and witherite were used; in the latter case complete decomposition only resulted after a second addition of witherite.

Decomposition of Sodium Nitrate by means of Calcium Carbonate.—Vessels of glass, porcelain, and wrought-iron were all acted on. A platinum boat heated in a porcelain tube was used, and although exact results were not obtained, as the boat was strongly attacked, yet the investigation shows that 1 equivalent of nitrate heated with 2.5 equivalents of carbonate is completely converted into caustic soda, and that the greater part of the nitric acid can be recovered. This appears to be a good process, if only suitable apparatus can be obtained.

Behaviour of Chlorates in Hot Solutions.—On passing chlorine into milk of lime, 5 molecules of chloride should be produced to 1 molecule of chlorate, but an excess of chloride is always found; this is commonly supposed to be partly due to the evolution of oxygen, especially on heating. Solutions of potassium chlorate were found to remain unchanged on boiling. A solution of calcium chlorate mixed with excess of calcium chloride, suffered no change in the chlorate on long boiling.

Preparation of Potassium Ferricyanide by means of Lead Peroxide.—The method proposed by Böttger (*Dingl. polyt. J.*, 1859, **151**, 430), in which ferrocyanide made strongly alkaline with potash, is boiled with lead peroxide, gives no ferricyanide if carbonic anhydride be excluded. Whereas Schönbein's method (*Dingl. polyt. J.*, 1857, **146**, 155) of boiling ferrocyanide solution with lead peroxide, carbonic anhydride being passed to neutralise the potash formed, quickly gives ferricyanide in quantity.

Preparation of Benzoic Acid from Benzoyl Trichloride and Water.—The conversion takes place in open vessels on boiling for about four hours, as well as in sealed tubes under pressure. J. T.

Composition of Weldon Mud and Similar Substances. By JEZLER (*Dingl. polyt. J.*, **239**, 74—78).—The author mentions that he has studied the recovery of manganese since 1875 (*ibid.*, **215**, 446), and found that after obtaining the recovered product in a solid form, the method generally in use in the Weldon process for examining the recovered product could no longer be applied. He states that his results appear to confirm Post's investigations, although they were not arrived at by the same mode of working. The recovery-product was found to contain varying proportions of binoxide of manganese, but always more than 2 mols. MnO_2 to 1 mol. base, the latter either as MnO or as a fixed lime. The recovery products, when not heated above 120° —a temperature which is not requisite for oxidation—show a higher percentage of water than that corresponding with the formula CaMnO_6H_2 . A product prepared on a large scale, according to Weldon's process, from partly slaked lime, showed distinct signs of unaltered lime particles. In order to determine the presence of a compound of lime and manganese in the product thus obtained, the author had to work out a method which admitted the separation of fixed lime from foreign lime. It was found that from such bodies suspended in water in a finely divided state fixed lime would be extracted as bicarbonate by treatment with carbonic acid, having previously saturated all foreign lime with carbonic acid. Unfortunately it has not been determined whether this decomposition was perfect. If such compounds fused in a glass tube are again suspended in water and heated with carbonate of calcium at 120° , free carbonic acid gas is evolved, and is said to emanate entirely from the carbonate of calcium used and to have been expelled by manganese dioxide. If such compounds (Weldon mud and the substances described by Gorgeu and Berthier) are exposed to the action of carbonic acid in the wet state, no reaction takes place, or if any it is but very slight. D. B.

Technology of Glass. By M. MÜLLER (*Dingl. polyt. J.*, **238**, 65—69).—When iron oxide is dissolved in glass, it gives a green colour only. In yellow, brown, and red enamels, where the colour is due to iron oxide, this is in a state of fine division. As soon as the oxide becomes dissolved, the green colour is produced and gas is evolved, probably oxygen.

In the preparation of white glass, a thick layer almost always has a pale green tint, due to a small amount of iron. By the addition of

manganese, this tint is removed. The admixture is so managed that the quickly cooled glass shows a pale rose tint; when slowly cooled, the glass is then colourless. Hence the effect of manganese cannot be the conversion of iron protoxide into peroxide. Not more than 0.1 per cent. of iron can be thus disguised. The manganese oxide is best added after the glass mixture has been run down, otherwise loss of decolorising power results from partial reduction of the manganese.

A glass containing 1 per cent. iron protoxide and 6 per cent. manganese protoxide, when heated in a stream of oxygen, became deep orange-red, and in a thick layer was perfectly opaque. On fusing in a stream of hydrogen, the colour passed through pale brown to very pale yellow, and the glass became perfectly transparent.

J. T.

Composition of Clay for Porcelain. By H. SEGER (*Dingl. polyt. J.*, 238, 169—173, and *Thonindustriezeitung*, 1880, 157 and 165).—With respect to the separation of clay substance by means of hot concentrated sulphuric acid, it may be noted that felspar is also somewhat attacked. Pure Norwegian felspar, on being heated for 15 hours with concentrated sulphuric acid, lost 3.59 per cent., which was made up of 0.55 per cent. potash, 0.62 per cent. alumina, and 2.4 per cent. of silica.

Analyses of numerous mixtures for porcelain are given.

Ground pegmatite is used as glaze for the Belgian and French porcelain given.

J. T.

Contributions to the Knowledge of Clay and Earthenware Goods. (*Dingl. polyt. J.*, 238, 344—349).—Schumacher mentions that for Germany it is preferable to use “dry mixings” in the manufacture of earthenware. However, if clays rich in sand are employed, they are mixed in the wet state. According to Limbor, the destruction of fire-bricks in German blast furnaces is due mostly to the presence of alkalis, and not so much to the deposits of carbon.

According to Kosmann, the action of coke-slugs on fire-bricks is important in cases where generators are used, and it is desirable that manufacturers should consider the composition of the ash of the coals when such furnaces are used.

In the generators of Müller and Eichölbrenner, the coke from the gas-coal of the Gelsenkirchen Riviers was burnt. This contains 11.92 per cent. of ash of the following composition:—

	Ash.		Slag.
	Soluble in H ₂ O.	Total.	
SiO ₂	—	47·91	62·95
Al ₂ O ₃	—	30·17	25·23
Fe ₂ O ₃	—	12·16	—
FeO	—	—	3·12
Mn ₂ O ₄	—	0·38	—
MnO	—	—	0·28
CaO	0·24	1·41	0·46
MgO	0·41	1·22	0·92
Na ₂ O	0·20	2·60	0·82
K ₂ O	0·26	3·34	3·51
SO ₃	0·84	0·82	—
P ₂ O ₅	—	—	0·55
Fe	—	—	0·09
FeS	—	—	0·04
	1·95	100·01	99·97

The aqueous extract represents a basic mixture of sulphates; the residual silicate corresponds with the formula $2\text{RSiO}_3 \cdot 5\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{SiO}_2$; whereas the analysis of the slag gives the formula



The slag contained small globules of metallic iron: thus, part of the iron is reduced to the metallic state in the generator; the sulphates of calcium and magnesium are volatilised, and the alkalis reduced to slag.

Michaëlis describes the preparation of artificial paving stones in the *Thonindustriezeitung* (1880, **123**, 268). In the present paper he refers to the properties these stones should possess, so as to be durable, laying special stress on the difficulty of breaking genuine stones by blows with a hammer. The stone, when it breaks, should not split into more than one or two large pieces.

D. B.

Zinc Distillation. By F. FISCHER (*Dingl. polyt. J.*, **207**, 387—392).—The author describes convenient apparatus for gas analysis and analyses of gases taken from zinc-reduction tubes at Letmathe:—

	CO ₂ .	CO.	CH ₄ .	H.	N.
Just before distillation began	15·58	38·52	4·17	41·70	trace
Distillation beginning, upper series	0·48	—	—	—	—
After some time, upper series	1·06	92·16	trace	5·32	1·01
„ „ lower series	0·11	97·12	trace	1·83	0·41
„ „ „	1·10	—	—	—	—
Distillation almost ended	0·82	98·04	—	0·72	trace

Two analyses of gases from muffles at Münsterbusch during strong distillation gave as follows:—

	I.	II.	
CO ₂	0·09	0·11	
CO	95·36	97·42	
CH ₄	trace	—	
H	3·72	1·20	
N	0·61	0·92	J. T.

Dephosphorising Pig-iron. By F. FISCHER (*Dingl. polyt. J.*, **238**, 416—424).—This paper gives a historical account of the researches made by various chemists in reference to the dephosphorisation of iron since 1830.

Karsten (*ibid.*, **130**, 154), Tanoyer (**123**, 441; **137**, 293), and others (**168**, 462), found that a large addition of lime in the blast furnace process withheld the sulphur to a great extent, retarding the passage of phosphorus into the pig-iron. According to Stein (*ibid.*, **227**, 106), cyanide of ammonium removes phosphorus from phosphiferous iron or iron ores, forming phospham, PN₂H, which is taken up by the slag rendered basic by adding magnesite, dolomite, witherite, or bauxite to the charge. This method has not yet proved practically useful, and the experiments as to the separation of phosphoric acid from the ores before refining, be it either by treatment with water (*ibid.*, **65**, 234), or by extraction with hydrochloric acid according to Stromeyer (*ibid.*, **175**, 404), or with sulphuric acid (Jacobi, *ibid.*, **201**, 245; **230**, 275), showed that these processes were too costly. It has hitherto been possible to separate the phosphorus only from the refined iron.

Wall, Winkler, and Fleury (*ibid.*, **129**, 420; **161**, 305; **163**, 188; **162**, 314—427) pass an electric current through the liquid iron.

Guest and Evans (**84**, 46) pass steam through the puddling furnace with a view of separating phosphorus and sulphur. This method has been improved by Nasmyth, Weniger, Parry, and others, who use superheated steam. Jordan, however, found that this process did not fulfil its original expectations. Other similar proposals have been made by Schafhäubl for smelting the metal in an atmosphere of chlorine; Audincourt, adding bleaching powder; Parker, adding bleaching powder and mineral oil; Scherman, adding iodine and alkaline iodides; but all without success. The use of calcium fluoride recommended by Wernecke and Cavan has been more successful (*ibid.*, **166**, 138; **188**, 472).

Engelhart and Knowles (**59**, 317; **149**, 317) tried to oxidise the impurities in pig-iron by fusing with nitrate of potassium; Southall and Crudgington (*ibid.*, **94**, 210) recommend to add borax, alum, and sulphur to the mixture, besides soda and potash; whereas Low (**96**, 80) used a mixture of nitrate of potassium, binoxide of manganese, and charcoal. Heaton, Hargreaves, and Bessemer (**186**, 489; **190**, 465; **191**, 144, 459; **187**, 480; **190**, 32; **191**, 216; **195**, 126) proposed similar methods, all of which were abandoned after a short time.

The action of the oxides of iron and manganese, however, appears to exercise a more beneficial influence in removing the impurities contained in pig-iron; a process depending on this action was

patented by Andre in 1879. In addition to the above, the use of lime, dolomite, and fluorspar was recommended. The process adopted by the *Gutehoffnungshütte in Oberhausen* was undoubtedly practically the most successful. In the puddling process, the slag from blast furnaces, or Bessemer or cupola furnaces was used, which is known to be rich in manganese and lime, and free from phosphorus. Until 1831, the hearth of puddling furnaces was made with sand; thus the slag was rich in silica, which retards the combustion of the silicon and hinders the separation of phosphorus. Hence the refining process was inserted, which was again superseded, when furnaces with slag hearths were introduced and fluxes of oxide of iron and lime added. The reaction which takes place is well known. During the examination of this process, the author had occasion to investigate the gases from puddling furnaces heated by a direct coal fire, the metal refined being very rich in phosphorus. It was found that oxygen was always present in considerable excess.

In 1856 Bessemer patented his well-known process of preparing steel and bar-iron from fluid pig-iron without the use of combustibles. However, it was soon noticed that phosphorus and sulphur were not attacked by the new mode of treatment. In order to act on these, Bessemer (*ibid.*, **143**, 105; **175**, 294) passed hydrocarbons, hydrogen, or steam through the decarburised iron at the end of the process, but without success.

Fuchs (**65**, 201) and Crawshaw (**186**, 244) succeeded in separating phosphorus by the use of a lime slag in the puddling process; Tissier (**146**, 118), Eaton (**159**, 371), Drown (**231**, 544), and Warner (**216**, 490) used soda; Snelus (**208**, 463; **234**, 311) used a lime-lining in the converter; whereas Siemens (**234**, 312) used a lining of magnesia and bauxite, and Rochussen and Daelen (**209**, 416) lined their furnace with oxide of iron. Bell (**225**, 264, 351; **229**, 184, **290**) and Stead (**230**, 278) from their experiments concluded that in all of these cases the temperature influences the success of the operation considerably. Troost (**186**, 420) and Snelus (**208**, 463) mention that the separation of phosphorus depends chiefly on the basicity of the slag. The researches of Krupp (**233**, 44) and Thomas and Gilchrist (**232**, 451; **233**, 46; **234**, 308) confirm this statement. The high temperature in the Bessemer converter does not appear to hinder the separation of phosphorus, provided the slag contains less than 20 per cent. of silicic acid, and the quantity of phosphoric acid it has to absorb does not exceed 12 per cent.

Harmet (**234**, 312) has patented the following process:—The silicon and carbon are first eliminated from the pig-iron, using the ordinary acid lining in the converter; the iron is then transferred to a second converter with a basic lining, the slag being retained in the first converter. Neither this process, nor that of Osann (**230**, 511) seem to have been practically successful as far as is known.

The experiments made with a view of improving the lining of the Bessemer converter appear to be more important. Ponsard, like Riley (**234**, 311), mixes powdered slaked lime with 10 to 30 per cent. graphite and 10 per cent. fireclay in a moist state and presses the mixture into bricks, which are afterwards dried and heated. Crossley

prepares a basic lining with lime and dolomite, or lime and ferric oxide, adding 5 to 20 per cent. of aluminate of sodium to the mixture as a "binding agent."

The *Bochumer Verein für Bergbau und Gussstahlfabrikation* uses a mixture of caustic lime or slaked lime or dolomite and litharge, red lead, bin oxide of manganese or chloride of manganese, and the requisite quantity of water to enable the mixture to be formed into bricks, which are dried and heated.

Jungmann and Uelsmann recommend the use of chlorides as "binding agents."

The *Actienverein Gutehoffnungshütte in Oberhausen* prepares bricks for lining furnaces by mixing bauxite with bole, slaked lime, or dolomite, and pressing the mixture into brick-forms. D. B.

Slag obtained during the Dephosphorising of Iron. By W. POCHIN (*Bied. Centr.*, 1880, 770).—The slag was first converted into a superphosphate by sulphuric acid, then powdered, and part of the iron and lime removed by hydrochloric acid. The results were as follows:—

SiO ₂	13·81	9·50
P ₂ O ₅	7·38	9·76
Fe ₃ O ₄	6·92	9·28
CaO	57·87	59·35, &c.

E. W. P.

Boiler Incrustation. (*Dingl. polyt. J.*, 237, 392—396).—A boiler in which the plates were overheated was found to have an incrustation over which lay a flocculent deposit, the latter being so greasy that it was not wetted by water. Ether extracted a fatty mass from the deposit, but much less from the incrustation. Analysis gave—

	Deposit.	Incrustation.
CaCO ₃	66·51	52·12
MgCO ₂	19·55	22·55
Fe ₂ O ₃ and Al ₂ O ₃	7·75	19·11
Insoluble	4·45	7·03
	<hr/> 98·26	<hr/> 100·81

In a boiler near Düsseldorf a deposit 6 cm. thick formed on the first plate of the right-hand furnace tube. A yellow powder was deposited at the bottom of the boiler. These were analysed, as also the incrustation on the left-hand tube and the feed-water.

	Powder.	Left tube.	Thick deposit.
CaO	50.92	35.28	35.36
MgO	0.92	6.14	5.76
Fe ₂ O ₃ and Al ₂ O ₃	0.75	0.52	0.81
SO ₃	2.16	42.40	44.12
CO ₂	38.83	4.48	3.90
Insoluble	2.24	3.55	3.67
H ₂ O at 130°	1.02	2.71	0.96
„ above 130°	0.63	3.26	2.61
Alkalis, organic, loss..	2.53	1.66	2.81
	100.00	100.00	100.00

The powder from all was easily wetted by water.

The feed-water contained per litre—

CaO.	MgO.	SO ₃ .	Cl.	N ₂ O ₅ .
0.186	0.011	0.071	0.025	trace

J. T.

Illuminating Power of Benzene, Toluene, Ethylene, and Ether. By KNUBLAUCH (*Ber.*, **14**, 240—246).—The author has experimented on the influence of the introduction of known quantities of benzene, toluene, ethylene and ether, on the luminosity of coal-gas, and finds that the illuminating power depends on the number of atoms of carbon liberated.

W. C. W.

Products from the Manufacture of Petroleum Gas. By W. RUDNEW (*Dingl. polyt. J.*, **239**, 72—74).—In Russia, and especially in the vicinity of the River Volga, the preparation of gas from petroleum is carried on very extensively, as it is found that owing to the low price of petroleum, gas can be made more cheaply from this than from coal. In making gas from petroleum a considerable amount of tar is obtained.

At the gasworks in Kasan 491,400 kilos. of petroleum from Baku are consumed annually in the production of gas; the yield of tar varying between 13,100 and 16,380 kilos. The latter is liquid, and gives by distillation—

1. Benzene: colourless liquid; sp. gr. 0.875 at 19°, yielding a distillate of 94 per cent. between 80° and 100°.

2. A mixture of benzene and toluene: colourless liquid; sp. gr. 0.870 at 19.5°, boiling at 80°, yielding 64.6 per cent. between 80° and 108°, and 26.9 per cent. between 100° and 120°. The tar is very rich in light hydrocarbons.

3. Naphthalene. The tar contains about 5 per cent. of this.

4. Anthracene. At the present time the distillation is not carried beyond a temperature of 270°, when the whole of the naphthalene distils over; it was found, however, that at this stage the temperature rises very rapidly to 350°, after which a distillate consisting of a thick green oily liquid is obtained. On cooling, this oil deposits solid hydrocarbons consisting mainly of anthracene.

It is a remarkable fact that the tar is almost entirely free from phenolic bodies.

D. B.

Commercial Petroleums. By OGLOBLINE (*Bull. Soc. Chim.* [2], 34, 682).—Although the sp. gr. of the American petroleum is less than that of the Caucasian, the former contains a greater proportion of heavy oils. Both varieties emit inflammable vapour at so low a temperature, that their use in the crude state is attended with danger. The Caucasian oil is not more difficult to purify than the American, and it is superior to the latter as an illuminating agent. As far as expense and intensity of light are concerned, the Caucasian oil burns better with a flat wick, the American oil with a round wick; the height of the end of the wick above the surface of the oil has a much greater effect on the illuminating power of the latter than on that of the former. C. H. B.

Use of Maize in the Preparation of Starch, Sugar, Spirit, and Beer. (*Dingl. polyt. J.*, 238, 488—493).—Although the proposals made by Polas, Pelouze, Biot and Soubeiran (*ibid.*, 63, 165; 94, 326; 86, 215; 86, 213) to obtain the sugar from the maize-plant have not been of practical value, Riche appears to have succeeded in abolishing the extraction of starch from potatoes and wheat to a great extent by working up maize for starch. Maize-grain has the following composition:—

Water.	Starch.	Albumin.	Oil.
17.10	59.00	12.80	7.00
Dextrin and sugar.	Woody fibre.	Ash.	
1.50	1.50	1.10 = 100.00	

In order to obtain the starch, the short fermentation process with water or water containing soda is used. The treatment with dilute soda-lye (2° to 3° B.) is customary in the north of France and in England. Stronger lyes occasion loss of albumin.

In order to prevent the rapid destruction of maize-flour, in consequence of the presence of an oil easily rendered rancid, Chiozza proposes to treat maize with dilute sulphuric acid.

To convert maize-starch into sugar, the apparatus recommended by Colani and Krüger is not practical, as the mixture of starch and acid water is a bad conductor of heat, so that in a large apparatus that part nearest to the sides of the vessel is converted into sugar or even caramellised before the middle part has been dissolved.

Bardy, Boulogne, Dusart and Gibon have surmounted this difficulty by introducing the mixture in thin layers.

According to Theissen's patent, maize-grain is steeped in water, then squeezed between rollers and the mass drenched in a sieve with water. The liquid starch which runs through, is used in the preparation of spirit, whereas the residue on the sieve is pressed into cakes, and forms an excellent fodder.

In order to malt maize, Kohn proposes to soak it in water, occupying four or five days in the winter and twenty-six to thirty-six hours during the summer months. It is then placed in layers and kept at rest until it heats and begins to sprout. As soon as the bed has become sensibly hot, it is turned over.

With regard to the commercial value of maize, Delbrück reports that the amount of water in Roumanian maize varies from 13·6 to 23·8 per cent.; starch 54·2 to 58·7 per cent. American maize contains about 58 per cent. starch. The value appears to depend on the consistency of the husks, seeds with thick husks containing less starch than thin husks. Mexican maize contains 4·8 to 5·8 per cent. fat and 49 to 49·5 per cent. starch. As a rule maize decorticated by boiling in the "*first mash vat*" gives a very small yield of spirit.

In conclusion, the mashing process is more fully dwelt upon by Delbrück in the original paper, a complete sketch of the apparatus used in each of the operations being given. D. B.

The Decrease of Nitrogen in Malt Wort during Fermentation. By H. GRIMMER (*Ber.*, 14, 140—144).—During a five days' fermentation of malt wort, the yeast produces about 10 times its weight of alcohol, and removes 7·76 per cent. of nitrogen from the liquor. After the beer has been in the barrels several months, a slight increase in the amount of nitrogen is frequently observed. W. C. W.

Treatment of Must in the Press House. By P. SEUCKER (*Bied. Centr.*, 1880, 761).—The quality of a wine is often spoilt in the press house, as so much depends on the treatment of the must. Generally the grapes are allowed to remain for some time before they are pressed, and no attempt is made to improve the quality of the resulting wine. This, however, can be done by treading out the grapes, as well as by separating the forerunnings from the second pressings.

The experimental results show that when the grapes are of medium or poor quality, the adoption of either of the above methods is to be strongly recommended; and whilst the cost of the former is but little more, the latter does not increase the expense at all.

E. W. P.

Wines from Cloudberry and Cranberry. By C. O. CECHE (*Dingl. polyt. J.*, 238, 174—176).—An essential distinction between these fruit wines and grape wines is the much smaller amount of extractive matter in the former, a difference largely due to the longer time the grapes are left on the plants after coming to maturity, whilst the berries are gathered when quite fresh.

Cloudberry (*Rubus chamæmorus*) wine is dark amber-yellow, very sweet, the taste of citric acid being very perceptible. Acids and alkalis do not change its colour; lead acetate gives a yellowish-white precipitate. Its analysis is given under (I):—

	I.	II.
Specific gravity	1·04	1·03
Extract	1·12 p. c.	1·04 p. c.
Ash	0·13 "	0·15 "
Alcohol	1·15 "	0·80 "
Sugar	6·15 "	5·10 "
Acid	0·80 "	1·20 "
Tannin	— "	traces

Cranberry (*Vaccinium oxycoccos*) wine has an amaranth colour. Nitric acid turns it yellow; with ammonia it remains red, but with a greenish shade; with soda it becomes green; and with lead acetate it gives a light grey precipitate. It has a sweet taste, in which citric acid is observable. Its analysis is given under (II). J. T.

Spontaneous Changes in Raw Sugars. By U. GAYON (*Compt. rend.*, 91, 993—995).—The paper relates to the spontaneous transformation of portions of crude crystallisable sugar into reducing sugar under the influence of some inverting ferment. The author finds that whilst borax, sulphurous acid, and calcium bisulphite are ineffectual in preventing this transformation, on the other hand, sodium salicylate, and sodium or potassium acetate, maintain the sugar in its original state, and he suggests that these agents may be applied industrially. R. R.

Composition and Unwholesome Effects of a Potato Sugar. By J. NESSLER (*Landw. Versuchs.-Stat.*, 26, 207—211).—A sample of potato sugar used for the purpose of strengthening weak wines was found on analysis to contain 26 per cent. of unfermentable substance, and the question arose whether this had any connection with the evil after-effects consequent on the consumption of large quantities of such wines. Experiments were therefore instituted with a view to settle this question; in one case the author imbibed the unfermentable constituents of 200 grams of potato sugar in one day, and at another time his assistant took half the quantity: in both cases unpleasant consequences followed, headache, vomiting, and cold perspiration ensuing, whereas the unfermentable components of cane-sugar did not produce any evil effect. J. K. C.

Dry Distillation of Wood. By E. FISCHER (*Dingl. polyt. J.*, 238, 55—57).—100 kilos. beechwood give about 45 kilos. vinegar (with 4 kilos. acetic acid and 1.1 kilos. of wood spirit), 23 kilos. charcoal, and 4 kilos. tar, with 28 kilos. of gas of the following average composition:—

CO ₂ .	CO.	CH ₄ .	H.	H ₂ O.
20.0	7.0	0.5	0.05	0.45

Owing to the large amount of carbonic anhydride and water present its practical value does not appear to be high. J. T.

General and Physical Chemistry.

Observations on a Group of Rays in the Solar Spectrum.

By L. THALLON (*Compt. rend.*, **91**, 368).—These observations were made with a view to ascertain whether the movement of the source of light could modify the wave-length of the rays emitted. The group of rays chosen consisted of two iron lines, *b*, *c*, on the outside of each of which is a telluric line, *a*, *d*. When the slit of the spectroscope is directed upon the centre of the sun's disc, the distances *a*—*b* and *c*—*d* are apparently almost equal ($= 0.25$ and 0.24 respectively).

Suppose the slit to be directed upon the eastern edge of the sun's disc. If the above theory be correct, the iron lines will now be shifted from left to right, while the telluric rays will be stationary, the distance *a*—*b* be 0.29 , and the distance *c*—*d* 0.20 . This expectation was strictly fulfilled, a corresponding effect being produced by directing the slit upon the western edge of the sun.

C. W. W.

Measurement of the Intensity of some Obscure Rays of the Solar Spectrum. By GOUY (*Compt. rend.*, **91**, 383).—By the method previously described (*Compt. rend.*, December, 1879), the author has measured the intensities of three rays (unity is one ten-millionth of a millimeter). The ray *c* has an intensity of 1.1 ; the ray *b* has an intensity of 0.9 , and the ray 4957 (Ångström) one of 0.45 .

The measurement of the intensities of the rays of the Group B (between 6866 and 6880) conclusively shows that these rays are atmospheric.

C. W. W.

Refraction Equivalents of the Diamond and of Carbon Compounds.

By J. H. GLADSTONE (*Chem. News*, **42**, 175).—The specific refraction of a substance, which has for some time been recognised as an important physical property, promises now to be of great service to chemists in deciding the rational constitution of many compounds. The refraction equivalent of a substance is the specific refraction multiplied by the atomic weight. The refraction equivalent of crystallised carbon or diamond is 5.0 , and that is the value of this element in the large majority of its compounds; but in certain cases, as, for instance, the whole of the aromatic series, the carbon has a higher refractive value. Brühl has put forward the theory that whenever there is a double linking of the carbon-atom, the refraction equivalent is raised by about 2.0 . The author supports this view, but contends that it fails to explain several other cases of high specific refraction, as *e.g.*, the essential oils, which give refraction-equivalents about three above the normal; the compounds containing cinnamyl; and especially the hydrocarbons which are richest in carbon. It is remarkable that, whereas the refraction of the carbon increases rapidly in these hydrocarbons as the proportion of hydrogen diminishes, it has only the normal value in diamond where there is no hydrogen at all.

D. B.

Influence of Change of Temperature and Pressure on Double Refraction. By F. PFAFF (*Jahrb. f. Min.*, 1880, 1, Ref. 151).—The author's method consists in observing the shifting of the coloured bands produced by alteration of temperature in wedge-shaped plates illuminated by parallel polarised light. By rise of temperature, the refractive indices of the ordinary and extraordinary rays are altered in different degrees. An increase or decrease of the difference between the two rays—that is to say, an increased or decreased double refraction, is indicated by a shifting of the bands towards the thin or thick end of the wedge respectively. A rise of temperature of 200° produced the following effects:—

I. *Optically Uniaxial Crystals*.—A. Shifting of the bands towards the thick end: quartz. B. Towards the thin end: vesuvian, beryl, apatite. C. No perceptible alteration: calcite, dolomite, chalybite, tourmaline, mellite, potassium ferrocyanide, zircon, and tinstone.

II. *Optically Biaxial*.—(1.) Rhombic crystals. A. Shifting of the bands towards the thick end: arragonite (\perp to the median line); celestin (\perp to the axis c). B. Towards the thin end: topaz, celestin, and heavy spar, all cut at right angles to the first median line. C. Alteration none or scarcely perceptible: anhydrite, topaz, arragonite, witherite, and cerussite.

(2.) Monoclinic crystals. In adularia ($\parallel M$) and mica the bands are shifted towards the thin end; in gypsum ($\parallel \infty P \infty$) towards the thick end.

(3.) Triclinic crystals, *e.g.*, albite, oligoclase, labradorite, anorthite, axinite, cyanite, and cupric sulphate exhibited no alteration.

An alteration in the length of the axis of elasticity by heating was directly observed in cleavage-laminae of gypsum. The position of extinction with crossed Nicols was altered to the amount of 5° when the lamina was heated till it began to give off water.

To observe the influence of pressure, the crystalline wedges were introduced into a strong glass cylinder containing water, and uniformly compressed on all sides by a pressure of 40 atmospheres exerted on the surface of the water. Bitter spar, calcspar, celestin, heavy spar, and gypsum exhibited a distinct shifting of the bands in the same direction as that which was produced in the same crystals by lowering of temperature. The degrees of susceptibility to heat and to pressure were, however, by no means equal, some crystals which were very sensitive to heat being quite insensible to pressure, whereas others which were sensitive to pressure were insensible to heat. H. W.

The Unit in Absolute Electrical Measurements. By LIPPMANN (*Compt. rend.*, 92, 183—186).—The absolute electromagnetic units of resistance and capacity, and the formulæ for passing from an absolute electromagnetic to an absolute electrostatic system, are independent of the choice of the unit of force. The units of intensity and electromotive force on the other hand depend on the unit of force. The *dynes* possesses special advantages only in the case of the determination of magnetic intensity by the method of oscillations; moreover, it complicates the formulæ for passing from one system to another, necessitating the use of a factor, and thus nullifying the advantage of a decimal system. This difficulty might be obviated, and perhaps the adoption of

a universal system of units facilitated, by taking as the fundamental units of time, distance, and force, the second, the meter, and the gram.

C. H. B.

Theory of the Galvanic Couple. By F. EXNER (*Wien. Akad. Ber.* [2], 82, 376—424).—The object of this paper is to replace the contact theory of the voltaic pile by a chemical one.

It is a well-known fact that a chemical reaction takes place between two substances with evolution of heat when the potential chemical energy of the components is greater than that of the products, and the heat evolved is the equivalent of the energy lost. For example, the arrangement $\text{Zn} + \text{H}_2\text{O}$ represents a greater potential energy than $\text{Zn} + \text{OH}_2$, and the result is the decomposition of the water by the zinc, with evolution of heat. Similarly the potential energy of $\text{Zn} + \text{CuSO}_4$ is greater than that of the products of the reaction $\text{ZnSO}_4 + \text{Cu}$, &c., and the energy lost in the reaction will appear, according to the arrangement of the experiment, either as heat or electricity. When zinc dissolves in water, the chemical energy which is lost reappears as positive and negative electricity, and when a maximum is reached these reunite and appear in the form of heat.

G. T. A.

Influence of Concentration of the Solutions on the Electromotive Force of Daniell's Cell. By J. v. HEPPEGER (*Wien. Akad. Ber.* [2], 82, 326—341).—The Daniell's element used in the experiments consisted of two beakers, one of which contained a zinc plate and a titrated zinc sulphate solution (of 50 to 10 per cent.), the other a copper plate and copper sulphate solution of sp. gr. 1.173. Communication between the two beakers was made by an inverted U-tube, 4 decimeters long, closed at the end with porous (?) earthenware plates, and filled by means of an opening at the bend with a solution of zinc sulphate of the same concentration as that in the beaker. A Siemens' resistance cell and Edelmann's reflecting galvanometer were included in the circuit, and the readings were made by a telescope provided with a scale, and placed at the distance of 2 meters. Taking the electromotive force, E_{50} , of a circuit, in which the zinc electrode is immersed in a mixture of equal parts by weight of water and zinc sulphate, or a 50 per cent. zinc sulphate solution as unity, the following values were obtained: $E_{50} = 1.000$, $E_{40} = 1.006$, $E_{30} = 1.010$, $E_{20} = 1.014$, $E_{10} = 1.020$.

Moser's results (*Wiedemann's Annalen*, 3, 216) agree with the authors.

The following table gives values representing the influence of the concentration of the solutions in a Daniell's element:—

Solution of Copper Sulphate at 18.5° C.

	At 18° C.	Saturated.	30 p. c.	25 p. c.	20 p. c.	15 p. c.	10 p. c.	5 p. c.	1 p. c.
Solution of zinc sulphate	Saturated.	1.000	0.998	0.997	0.995	0.992	0.989	0.984	0.971
	60 p. c.	1.004	1.002	1.001	0.999	0.996	0.993	0.988	0.975
	50 p. c.	1.010	1.008	1.007	1.005	1.002	0.999	0.994	0.981
	40 p. c.	1.016	1.014	1.013	1.011	1.008	1.005	1.000	0.987
	30 p. c.	1.020	1.018	1.017	1.015	1.012	1.009	1.004	0.991
	20 p. c.	1.023	1.021	1.020	1.018	1.015	1.012	1.007	0.994
	10 p. c.	1.030	1.028	1.027	1.025	1.022	1.019	1.014	1.001
	1 p. c.	1.041	1.039	1.038	1.036	1.033	1.030	1.025	1.012

By using one metal and two solutions of its salts of different degrees of concentration, the following results were obtained:—

With solutions of magnesium sulphate (the electromotive force expressed in thousandths of a Daniell's element)—

10 per cent.	20 per cent.	30 per cent.	40 per cent.	50 per cent.
5 per cent. + 6	0	—13	—23	—30

where the negative numbers show that the current proceeded from the stronger to the weaker solution.

With zinc sulphate—

	30 per cent.	5 per cent.
10 per cent.	—20	0
30 „	—	+ 21

In both these cases mercury was used for the electrodes, and it is curious that whilst in the zinc and zinc sulphate circuit the current proceeds from the weaker to the stronger solution, in the magnesium and magnesium sulphate circuit, it proceeds from the stronger to the weaker solution.

G. T. A.

Measure of the Thermo-electric Electromotive Forces developed by the Contact of a Metal and a Liquid. By E. BOUTY (*Compt. rend.*, 90, 917).—The author has measured the electricity developed when two similar plates of the same metal are immersed in two portions of a liquid (a salt of the metal) kept at different temperatures.

The following table gives the results in terms of a Daniell. The hot metal is, in these cases, the positive:—

Metal.	Liquid.	Electromotive force for a diff. of 1° Da.	Mean for each metal.
Platinum....	Platinic chloride	0·000735	0·000735
Copper	Cupric sulphate.....	0·000688	0·000696
	„ nitrate	0·000704	
Zinc, amalga- mated	Zinc chloride (sp. gr. 1·05— 1·5)*	0·000677	0·000705
	„ sulphate	0·000696	
	„ nitrate	0·000692	
	„ acetate	0·000756	
Cadmium ..	Cadmium chloride	0·000615	0·000616
	„ sulphate	0·000598	
	„ nitrate	0·000634	
Mercury	Mercurous nitrate.....	0·000140	0·000140
Gold	Auric chloride	0·000024	0·000024
Iron.....	Ammonia, sulphate of iron..	—0·000024	0·000002
	Ferrous sulphate	0·000000	
	„ chloride	+0·000077	
	„ acetate.....	+0·000087	
	„ tartrate	—0·000127	

* Stronger solutions give different results; these will be described in a future communication.

It will be seen from these numbers that salts of the same oxide give nearly the same number; also that the numbers for copper and for amalgamated zinc are nearly identical, from which it follows, that the electromotive force of a Daniell cell is invariable for all temperatures.

When the cold metal is the positive element, the results are very irregular. The metal is frequently attacked, and the oscillations of the electrometer vary from $\frac{5}{1000}$ or $\frac{6}{1000}$ of a Daniell up to a few hundredths. The following results are given as approximations:—

Metal.	Liquid.	Mean electromotive force for 1° (between 10° and 30° Da.		Mean.
Silver	Silver nitrate	—0·000165	}	—0·000202
	Silver-plating bath	—0·000240		
Iron	Ferric chloride	—0·00170	}	—0·00156
	„ nitrate	—0·00169		
	„ sulphate	—0·00149		
	Iron alum	—0·00134		
Nickel	Nickel chloride	—0·00208	}	—0·00214
	„ nitrate	—0·00234		
	„ sulphate	—0·00200		
Magnesium..	} Values greater than the above, but very uncertain.			
Aluminium..				

C. W. W.

Photo-electric and Thermo-electric Properties of Fluorspar.

By G. W. HANKEL (*Jahrb. f. Min.*, 1880, **1**, Ref. 331).—This paper contains the results of the author's observations on 24 crystals of fluorspar, including 10 green specimens from Weardale and Alston Moor in Cumberland, 6 violet-blue from the same localities, and others from Cornwall, and from Freiberg and Stolberg in the Harz. The crystal under examination was placed in a small copper box filled with copper filings, in such a manner that only one face, edge, or summit, remained uncovered, and was then exposed for a certain time to the light of a clouded sky, or to the direct rays of the sun, or to the electric light, the elevation of temperature sometimes produced in the last case being diminished, as far as possible, by the interposition of a solution of alum between the crystal and the source of light. To examine the photo-electricity produced by the irradiation, a platinum wire connected with a gold-leaf electroscope was brought as near as possible to different points of a face of the crystal not covered by the copper filings, and the divergence of the gold leaves thereby produced was observed with a microscope. Observations were also made on the electricity developed during the cooling of a crystal of fluorspar previously heated to 100°. The results are as follows:—

1. The effect of irradiation is to render the middle parts of the cubic faces of the crystal negatively electric (most strongly in the green crystals from Weardale), the electric intensity diminishing towards the edges of the faces, and there often passing into a weak positive charge. This photo-electric excitability increases at first with the duration of the illumination (the strongest effect being produced

by the electric carbon light), but diminishes if the crystal is exposed repeatedly, or for a long time, to the light. The electric state produced by the irradiation does not change into the opposite when the crystal is transferred to a dark room, but merely disappears gradually by dispersion and equalisation.

2. The thermo-electricity produced by cooling the crystals is opposite in sign to that developed by heating or by illumination, that is to say, as the fluorspar cools, the middles of the cube faces are positively electric, the edges and summits more or less negative. Consequently the electric states of fluorspar after illumination and during heating are identical so far as regards the quality of the electricity developed.

The limits between the positively and negatively electrified portions of the faces, either in the photo-electric or in the thermo-electric state, are not quite constant even in the same crystal. The ratio of the intensity of the photo-electricity to that of the thermo-electricity in different crystals is sometimes greater, sometimes less than unity.

H. W.

Laws of the Development of Electricity by the Action of Pressure on Tourmaline. By J. and P. CURIE (*Compt. rend.*, **92**, 186—188).—The crystals experimented with were prisms parallel with the principal axis. They were transparent, colourless, or but slightly coloured, and did not conduct electricity. Opaque or semi-opaque dark-coloured varieties conduct electricity, and consequently are not suitable for experiments of this character. The laws deduced were as follows:—

(1.) The two extremities of a tourmaline crystal develop quantities of electricity which are equal, but of opposite kind.

(2.) The quantity developed by a given increase of pressure is equal to that developed by an equal diminution of pressure, but is of opposite kind.

(3.) This quantity is proportional to the variation of pressure, is independent of the length of the tourmaline crystal, and for the same variation of pressure per unit area of surface is proportional to the surface.

These laws are similar to those deduced by Gauguin for the pyroelectric properties of tourmaline, and it is probable that both series of phenomena are due to the same cause, viz., the contraction or dilatation of the tourmaline crystal along its axis.

C. H. B.

Polar Electricity of Hemihedral Crystals with Inclined Faces. By J. and P. CURIE (*Compt. rend.*, **91**, 383).—In a previous paper (*Compt. rend.*, **91**, 294) the authors showed that whenever a hemihedral crystal with inclined faces contracts, electric poles are formed in a particular position; and that whenever the crystal expands electric poles are formed in the opposite direction.

With a view to ascertain the relation of these poles to the position of the hemihedral faces, the principal pyroelectric crystals were studied. It was found that the extremity of the axis of polar electricity, which is terminated by the hemihedral faces forming with it the most acute angles, becomes positive in contraction, and negative in expansion;

the opposite extremity, formed either without hemihedral faces or by the base, or by the hemihedral faces making the more obtuse angles with the axis, becomes positive in expansion, negative in contraction.

C. W. W.

Electrical Phenomena of Tourmaline and Hemihedral Crystals with Inclined Faces. By J. and P. CURIE (*Compt. rend.*, 92, 350—353).—Gauguin assumed that during a variation of temperature, a crystal of tourmaline was in the condition of a thermoelectric pile of great resistance and great electromotive force. This supposition agrees with the quantitative laws which he established, but does not explain the development of electricity by pressure, or the fact, which the authors have discovered, that this development takes place only on the bases of the prism, and not on the lateral faces. The authors suppose that between the opposed faces of two contiguous layers of molecules there exists a constant difference of tension, involving a condensation of electricity, which depends on the distance between the two layers. If by any cause, such as variation of temperature or pressure, this distance is changed, the quantity of electricity will vary. From this supposition it may be deduced that the quantity of electricity developed is proportional to the variation of distance between the layers of molecules and to the surface, but is independent of the number of layers, and consequently of the length of the crystal. All these laws have been previously established by experiment.

Tourmaline being a compound body, the difference of tension between two contiguous layers of molecules may be due to the different composition of different parts of a molecule, or it may be due simply to the form of the molecule. All crystallographic theories trace to the molecules themselves the dissymmetry shown by particular crystalline forms. The authors have shown that in all non-conducting hemihedral crystals that have been studied the nature of the development of electricity is connected with the form of the crystal in such a way that the extremity corresponding with the most acute solid angle is always negative on dilatation. This constant relation is probably not due to chance, and the analogies between the form of the molecule and the form of the crystal being admitted, it would appear that the acute extremity of a molecule always stands with regard to the opposed base of the succeeding molecule in the same relation as the zinc of a voltaic pile stands to the copper, *i.e.*, it is always charged with positive electricity. It would seem that the form of the molecule is of primary importance, and that the matter of which it is composed is of but little account.

C. H. B.

Preparation of Selenium Resistance Rods for Photophonic Purposes. By A. WEINHOLD (*Dingl. polyt. J.*, 239, 160).—The author gives a minute description of the preparation of these rods as used in photophones. They are made of small glass tubing a few centimeters in length and about 1.5 mm. in thickness, having two small spokes fused to each end, which serve as connectors for the wires. A double thread is cut into the tube by coating it with a spirally winding layer of sealing-wax, and exposing it to the action of an aqueous solution of

hydrofluoric acid for a few minutes. Small brass helices are then wound round the thread in opposite directions, and the narrow spaces intervening between the double thread are coated with selenium, an operation which requires great care to be successful. In the dark these rods are said to be equal to 300 to 500 Siemens units; with the light on one side they are equal to about half that quantity, and still less when completely exposed to light. By altering the dimensions it is of course possible to vary the power of resistance to almost any degree.

D. B.

Specific Magnetism of Ozone. By H. BECQUEREL (*Compt. rend.*, **92**, 348—350).—Ozone is more strongly magnetic than oxygen, and the ratio of the specific magnetism of ozone to that of oxygen is distinctly greater than the ratio of the density of the former gas to that of the latter.

C. H. B.

Specific Heat of Gases and Vapours. By N. FLAVITZKY (*Bull. Soc. Chim.* [2], **34**, 335—337).—This is a preliminary communication on a law of variation of the specific heat of gases or vapours with the temperature based on the thermodynamic principle, that the specific heat of a gas at constant volume consists of two factors, namely, the heat which serves to increase the movement of the molecule and that of the movement of rotation of the molecule or the atomic movement. Of these, the first is a function of the heat of expansion, and changes but little with change of temperature. According to the author the law which expresses the heat due to rotation at varying temperatures is given by the formulæ—

$$Pr = 0.92n \frac{\alpha''}{\alpha'} (1 + \alpha't) = 0.92n\alpha''T,$$

where P is the molecular weight, 0.92 the heat which increases the movement of rotation of a unit of weight or of an atom of hydrogen; α'' the coefficient of expansion of the gas or vapour at constant volume, α' the corresponding coefficient for hydrogen, T the absolute temperature from the absolute zero, which for hydrogen is -272.4°C . (α' being 0.003667).

From this it follows that at a temperature $T_1 = \frac{1}{\alpha''}$ the heat of movement of rotation of a gas or vapour is 0.92 n, which is the law of Naumann.

With respect to the specific heat at constant pressure, the following formula is given—

$$PCp = 1.922 \frac{\alpha'}{\alpha} + 2.998 \frac{\alpha'}{\alpha} + \alpha''n 0.92T \frac{\alpha'}{\alpha},$$

where Cp is the specific heat at constant pressure, α the coefficient of dilatation of the gas at constant pressure, and α' the same coefficient for hydrogen (0.003661). Other formulæ derived from this are given which allow of comparison with the experimental results obtained by Regnault, Wiedermann, and Wullner. The author has made use of these equations in order to calculate the coefficients of expansion of

certain vapours from the specific heats as experimentally determined, and finds that they increase with the molecular weight; moreover for low pressures the coefficients of expansion of gases and vapours at constant volume are equal to the coefficients of expansion at constant pressure.

C. E. G.

Cooling Power of Gases and Vapours. By WITZ (*Compt. rend.*, **92**, 405–407).—The cooling power of air under increased pressure has been determined (*ibid.*, **39**, 228), and at 760 mm. the rapidity of cooling in dry air is—

For an excess of	60°	0·0298°
„ „	40	0·0208

In dry and saturated atmospheres the following results have been obtained:—

		For an excess of	
		60°.	45°.
1st series	{ Dry air	0·0285	0·0189
	{ Moist air	0·0241	0·0187
2nd „	{ Dry air	0·0298	0·0207
	{ Moist air	0·0243	0·0208

It is seen that at 45° the rapidity is practically the same for both moist and dry air, but at 60° it is slightly less for moist air. The following results explain this. By connecting the cooling medium with a water manometer, it is seen that the pressure and temperature vary, rising rapidly at first to a maximum where it is momentarily stationary, and then slowly diminishing. For dry air, the temperature at the maximum, 61°, is 1·2° above that of the walls, and in the case of moist air the temperatures are 64° and 1° respectively. From these data, it is calculated that the rapidity of cooling in dry air = 0·1124, and for saturated air 0·1160. In a previous paper (this Journal, **36**, 432; *Ann. Chem. Phys.* [5], **15**, 433, 529), the author found by a different method that the rapidity in dry air was 0·1116, corresponding with the formula $V = (0·11 + 0·0016)\epsilon$.

The rapidity of cooling in sulphurous anhydride and coal-gas has been determined.

	For an excess of	
	60°.	45°.
Coal-gas saturated at 0·6°	0·119	0·063
Sulphurous anhydride at 15·5°	0·021	0·011

Compared with air, the mean cooling power of coal-gas is 3·48, and of sulphurous anhydride 0·61.

In steam at 100° the rapidity of cooling is—

For an excess of			
45°.	38°.	22·5°.	19°.
0·03	0·0227	0·0168	0·0217

The rapidity of cooling increases proportionally with the 0·83th

power of the excess; this explains the slight difference which occurs in the case of saturated air for an excess of 60° . L. T. O'S.

Cause of Variation of the Fixed Points of Thermometers. By J. M. CRAFTS (*Compt. rend.*, **91**, 370).—The author concludes from a large number of experiments that interior and exterior pressure have little or no effect in altering the zero points of thermometers. The only material cause in this alteration is the gradual contraction of the bulb after blowing, this contraction being facilitated by the increased mobility of the molecules of the glass produced when the thermometer is used at high temperatures (350 — 360°). In all probability this alteration could be minimised by sufficient annealing previous to graduation. C. W. W.

Double Decomposition in Absence of Water. By A. POTILITZIN (*Bull. Soc. Chim.* [2], **35**, 105).—By treating sodium, potassium, and silver bromides with hydrochloric acid gas, heat is absorbed, and chlorine is substituted for bromine, in the first case even at the ordinary temperature, the percentages of bromine replaced being 21.93, 11.8, and 4.26 respectively, numbers which are inversely as the atomic weights of the metals contained in the salts. This is another proof that the mutual reaction between two bodies is a function of the atomic weights of the metallic elements taking part in the reaction.

L. T. O'S.

Reciprocal Replacement of the Halogens. By BERTHELOT (*Compt. rend.*, **90**, 893).—The replacement of chlorine by bromine and of bromine by iodine is theoretically possible in those cases in which the heat evolved in the formation of the secondary compound (BrCl or IBr) is greater than the heat absorbed in the direct substitution, *e.g.*, the reaction $\text{I}_4 + \text{KBr} = \text{KI}_3 + \text{IBr}$ would evolve $-15 + 22.7 = +7.7$ (kil.-deg.). These replacements might also take place at temperatures at which the metallic chloride or bromide is dissociated, so that the reacting element would be able to unite with the free metal.

The author has repeated Potilitzin's experiments on the above reactions, but has taken precautions to exclude the action of oxygen, moisture, and the alkalis and acids of glass. Under these circumstances he finds that in no case does such a reaction take place up to a temperature of 400° . C. W. W.

Displacement of Chlorine by Bromine in Potassium Chloride in an Atmosphere of Nitrogen. By A. POTILITZIN (*Bull. Soc. Chim.* [2], **35**, 167).—In reply to Berthelot (preceding abstract), the author has repeated his own experiments by heating potassium chloride with bromine both in a tube free from air, and in a rarefied atmosphere of nitrogen, and in each case chlorine is replaced by bromine, showing that the replacement is not due to the oxygen of the atmosphere, or to any accidental circumstance. L. T. O'S.

Heat of Formation of Gun-cotton. By SARREAU and VIELLE (*Bull. Soc. Chim.* [2], **33**, 581—582).—The authors have studied the

decomposition of ordinary gun-cotton, $3\text{C}_6\text{H}_7(\text{NO}_2)_3\text{O}_5 + \text{C}_6\text{H}_8(\text{NO}_2)_2\text{O}_5$, under various conditions, and find that at pressures near that of the atmosphere the whole of the nitrogen is eliminated as nitric oxide, but at higher pressures it is reduced, and the sole products of combustion are nitrogen, hydrogen, carbonic oxide and anhydride, and water, the proportion of carbonic oxide and water decreasing with increase of pressure, whilst that of the carbonic anhydride and hydrogen increases. The heat of combustion of gun-cotton was found to be 1070 cal. per kilogram, and the heat of formation 542 per kilogram, or 620 per equivalent.

C. E. G.

Thermal Formation of Pyrogenic Hydrocarbons. By BERTHELOT (*Compt. rend.*, **92**, 266—267).—The formation of benzene from acetylene, $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$ (liquid) develops heat = + 178.3 cal., or + 59.4 cal. for each molecule of C_2H_2 condensed. Rechenberg has recently determined the heat of combustion of naphthalene and anthracene, and from his numbers the author has calculated the heat of formation of these hydrocarbons from acetylene. He finds that the production of naphthalene from acetylene, $5\text{C}_2\text{H}_2 = \text{C}_{10}\text{H}_8$, solid, + H_2 , develops heat = + 263.5 cal., or + 52.7 cal. for each molecule of acetylene. For naphthalene hydride or pentacetylene, $\text{C}_{10}\text{H}_{10}$, this number should be increased by about + 57 cal. The formation of anthracene from acetylene, $7\text{C}_2\text{H}_2 = \text{C}_{14}\text{H}_{10}$, solid, + 2H_2 , develops heat = + 312.7 cal., whilst the formation of anthracene hydride or heptacetylene, $\text{C}_{14}\text{H}_{14}$, would develop heat = + 355 cal. approximately. These numbers show the close relationship existing between the polycyclic hydrocarbons. So large a loss of energy explains the synthetic production of these hydrocarbons, their stability, and their relatively saturated characters.

C. H. B.

Apparatus for Showing the Dissociation of Ammonium Salts. By D. TOMMASI (*Compt. rend.*, **92**, 299).—The apparatus, to which the author gives the name “dissocioscope,” consists of a glass tube, from 20 to 25 cm. high, and 2 to 4 cm. diameter. In this tube is suspended, by means of a platinum wire, a strip of blue litmus-paper, moistened with a cold saturated solution of ammonium chloride or some other ammonium salt. The apparatus is placed in a glass vessel full of boiling water; the ammonium salt is at once dissociated, and the litmus-paper is coloured red. On cooling, the dissociated ammonia combines with the acid, and the blue colour of the test-paper is restored. It is evident that the experiment may be repeated any number of times.

C. H. B.

Passive State of Iron. By L. VARENNE (*Compt. rend.*, **90**, 998).—The commencement of passivity is always preceded by a variable amount of chemical action. In pure nitric acid, (HNO_3), the duration of the action is so short as to be imperceptible. In nitric acid of 42°B. , the action lasts for some seconds, and then ceases suddenly, after which the metal may be immersed, with proper precautions, even in nitric acid of less than 35°B. , without any action taking place.

The same phenomena are produced in nitric acid between 42° and 35° B., but in acid of less than 35° B. the action is intermittent.

Passivity may be induced in a rod of iron by the immersion of a part only in concentrated nitric acid, *i.e.*, a rod of iron, a portion of which has been rendered passive by immersion in strong nitric acid, may be transferred to dilute nitric acid without dissolving therein. The second immersion must be done with extreme slowness, or an action sets in immediately. The stability of this passivity is but slight, a very small movement of the rod in the acid being sufficient to set up an action.

The author explains these phenomena by supposing that the gas formed on the surface of the metal adheres to it and protects it. This explains the brilliant appearance of the metal, and the fact that iron in the passive state loses this property in a vacuum. C. W. W.

Rate of Solution of Magnesium in Different Acids. By KAJANDER (*Bull. Soc. Chim.* [2], **34**, 325).—The weight of metal dissolved in unit of time is, *ceteris paribus*, a simple function of the molecular weight of the acid, of its concentration, and of the nature (water, saline solutions, &c.) of the medium in which the reaction is effected. Heat accelerates the reaction only because it diminishes the internal friction of the liquid. J. M. H. M.

Part played by Time in the Formation of Salts. By BERTHELOT (*Bull. Soc. Chim.* [2], **35**, 228—231).—When an acid dissolved in water acts on a dissolved base or salt, or a dissolved base on an acid or salt, or two salts on one another, the products being equally soluble, and forming a homogeneous system, it can be proved that the time required for the reaction is no longer than that required for the complete mixing of the two liquids.

Certain doubts, however, exist with regard to the exact duration of saline reactions, but experiment removes them. For whenever a given system undergoes a slow chemical or physical change, such change can be detected by thermometric methods. *The heat evolved in a slow reaction is the difference between the quantities of heat evolved when the system of components and that of the products of the slow reaction are brought to the same final condition by the same reagent.*

Numerous applications of this theorem are found in the slow formation of ethers, amides, the electrical formation of ozone, &c. But in the case of saline reactions, time does not intervene, except in special cases where bodies may vary in their hydration and isomeric states. In general, the same method shows that these reactions take place and chemical equilibrium is established in an exceedingly short period of time. To apply it, the heats of formation of the two salts of the same base with different acids are measured, and also the heat evolved or absorbed by treating each salt (prepared for several months or years) separately, with the acid of the other salt; then the difference between the heats of formation of the two salts is equal to the difference between the quantities of heat taking part in the reciprocal reactions of the acids on the salts. This equality will only be true if the reactions are instantaneous, and the final state of the liquids identical,

for otherwise there will be thermal residues, showing that the reactions are incomplete, as has been proved in numerous cases by Thomsen and by the author. The same holds good for the reciprocal decompositions of salts by alkalis, and double decompositions of salts which do not precipitate one another.

Results obtained in this way agree with the actual determinations of the heats of neutralisation; moreover they agree amongst themselves, notwithstanding the difference of the conditions of temperature, concentration, relative proportion, &c., under which the reactions take place. There can, therefore, be no doubt that saline reactions take place almost instantaneously.

The chemical equilibrium so rapidly established in dissolved saline systems seems correlative with the electrical conductivity which characterises these systems.

L. T. O'S.

Inorganic Chemistry.

Atmospheric Ozone. By E. SCHÖNE (*Bull. Soc. Chim.* [2], **34**, 337—339).—The author remarks that up to the present day we have no clear and decisive proof of the presence of ozone in the atmosphere, all the reagents which have been used to detect it being equally affected by hydrogen peroxide, which the author's experiments have shown to exist in the atmosphere. He considers the ozonoscopes of Schönbein and Houzeau of no use in estimating the variation in quantity of ozone (or hydrogen peroxide), since the presence of moisture exercises so great an influence on the result, that the test-papers serve almost as well for rough hygrometers as for ozonometers. He proposes to substitute for iodised starch-papers, papers impregnated with hydrated thallium oxide. The variation in the amount of moisture does not affect the coloration of these thallium-papers, and after being exposed to the air they may be preserved without further change. Regular series of observations made with these papers in 1879 show that the intensity of coloration depends on: 1st, the time of day or night, the coloration being always more intense in the day than in the night; 2nd, the direction of the wind, the coloration being more intense with a south wind, especially in winter; 3rd, the presence of rain, clouds, &c., the coloration being faint in proportion as these are abundant. Nothing in his experiments contradicts the hypothesis that the coloration of the thallium-papers is produced entirely by hydrogen peroxide.
J. M. H. M.

Boiling Point of Chlorine Tetroxide. By G. SCHACHERL (*Annalen*, **206**, 68—75).—The boiling point of chlorine tetroxide has not hitherto been directly determined, on account of the explosive nature of the substance, but has been deduced from the tension of its vapour. The author shows, however, that the substance undergoes dissociation, rendering the exact determination of the tension impos-

sible. Euchlorine gas, free from hydrochloric acid, was condensed in a freezing mixture, and when the flask containing about 20 c.c. of the condensed mixture of chlorine tetroxide and free chlorine was placed up to the level of the fluid into water of 30°, the liquid boiled constantly at 9.9°, the barometric pressure being 730.9 mm. Provided that contact of the tetroxide, with organic substances, such as cork, indiarubber, &c., is carefully avoided, it can be distilled without risk of explosion.

O. H.

Action of Chlorine on Nitrogen Sulphide. By E. DEMARÇAY (*Compt. rend.*, 91, 854—856).—When the nitrogen sulphide of Fordos and Gélis is suspended in 3 or 4 times its volume of chloroform, and a current of chlorine passed into the mixture, it dissolves with development of heat. The red-brown solution on cooling deposits magnificent sulphur-yellow crystals of the compound SNCl , and a further crop may be obtained from the mother-liquors by concentration. It decomposes slowly in the cold, but more rapidly when heated, with evolution of nitrogen and formation of sulphur chloride, S_2Cl_2 , which combines with unaltered chloronitride, forming stable compounds: this change takes place rapidly at 100°.

In the preparation of sulphur chloronitride in the manner above described, the solution becomes olive-green, and then almost black, before it acquires the orange-brown tint which marks the termination of the action: this is due to the formation of a second chloride, $(\text{SN})_3\text{Cl}$. The best method of preparing this is to add the proper proportion of sulphur nitride to a solution of the chloronitride in chloroform, and heat gently until dissolved: on cooling, the new compound is deposited in long copper-coloured needles. It is less soluble in chloroform than the compound SNCl , and does not alter so readily. When strongly heated, it decomposes with a feeble explosion.

C. E. G.

Artificial Production of Crystallised Quartz. By C. FREIDEL and E. SARASIN (*Jahrb. f. Min.*, 1880, 1, Ref. 179).—Crystallised quartz has several times been prepared artificially: first, by Sénarmont, who obtained it by heating gelatinous silica with hydrochloric acid; then by Daubrée, by the action of superheated water on glass; and lastly, by Hautefeuille, who treated silica at 750—800° with sodium tungstate. The authors prepare it by heating to a temperature below dull redness in a closed steel tube lined with copper, a mixture of potash, alumina, and gelatinous silica, the last in excess, in presence of water. In this way, after continuing the heat, in one experiment for 14 and in another for 38 hours, they obtained the silica wholly or almost wholly crystallised.

The first experiment yielded numerous very regularly formed crystals of the ordinary quartz form (prism with the two rhombohedrons), which acted strongly on polarised light in the manner of native quartz. In the second experiment, the crystals were larger (up to 0.5 mm. long, and 0.1 mm. broad), but mostly broken off at one end. They sometimes had the form of more acute rhombohedrons, with indications of tetartohedral forms, and many of them exhibited striations and modes of aggregation well known in native quartz.

H. W.

Combination of Titanium Tetrachloride with Phosphorus Trichloride. By A. BERTRAND (*Bull. Soc. Chim.*, **33**, 565—566).—When titanium tetrachloride is mixed with phosphorus trichloride, small yellow crystals are formed on the sides of the vessel. These have the composition $\text{TiCl}_4 \cdot \text{PCl}_3$, and melt at 85.5° . C. E. G.

Action of Hydrochloric Acid on Metallic Chlorides. By A. DITTE (*Compt. rend.*, **92**, 242—244).—The solubility of calcium chloride in a solution of hydrochloric acid decreases as the concentration of the acid increases. When a current of hydrochloric acid gas is passed into a saturated solution of calcium chloride, and the latter is kept cool, crystals separate out of the composition $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. If fragments of fused calcium chloride are dissolved in concentrated hydrochloric acid in a vessel surrounded by cold water to prevent any considerable rise of temperature, the hydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ separates out on cooling. The same hydrate may also be obtained by passing hydrochloric acid gas over crystals of the hexhydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. It is very hygroscopic.

Strontium chloride behaves like calcium chloride, and gives crystals of the hydrate $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, when hydrochloric acid gas is passed into a saturated solution of the salt.

If hydrochloric acid gas is passed into a saturated solution of cobalt chloride, the temperature being kept nearly constant, the pink colour of the solution changes to deep blue-violet, and on cooling, beautiful needles of the same colour are deposited. They have the composition, $2\text{CoCl}_2 \cdot 3\text{H}_2\text{O}$. If a saturated solution of cobalt chloride is saturated with hydrochloric acid at 35° in presence of an excess of the salt, an amethyst-blue liquid is obtained, and this on cooling deposits needles of the same colour, which contain only 1 mol. of water, and have the composition $\text{CoCl}_2 \cdot \text{H}_2\text{O}$. Both these hydrates are very hygroscopic. The results of the author's experiments with these and other metallic chlorides are given in the following table:—

	H_2O .		HCl , saturated at 12° .	
	Salt dissolved. Per litre.	Crystals formed.	Salt dissolved. Per litre.	Crystals formed.
	Grams.			
Calcium chloride	700	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	270	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
Strontium "	500	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	20	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
Magnesium "	720	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	65	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
Cobalt "	415	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, red	205	$2\text{CoCl}_2 \cdot 3\text{H}_2\text{O}$, blue
" "	"	"	"	$\text{CoCl}_2 \cdot \text{H}_2\text{O}$, blue
Nickel "	600	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, green	40	$\text{NiCl}_2 \cdot \text{H}_2\text{O}$, green- ish-yellow
Manganese "	870	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, rose	190	$\text{MnCl}_2 \cdot \text{H}_2\text{O}$, white
Copper "	630	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, bluish-green	290	$\text{CuCl}_2 \cdot \text{H}_2\text{O}$, brownish-yellow

The solubility of potassium chloride in solutions of hydrochloric acid diminishes rapidly and regularly as the concentration of the acid increases, and the salt is almost insoluble in the strong acid. Its

solubility in the acid solutions increases as the temperature rises, and the anhydrous chloride separates out on cooling. Certain other chlorides behave in the same way: their solubility decreases regularly as the concentration of the acid increases. The following table gives the amount in grams of different chlorides dissolved in 1 litre (I) of water at 17°; (II) of a saturated solution of hydrochloric acid at the same temperature:—

	I.	II.
Potassium chloride.....	35.0	1.9
Ammonium „	33.7	3.7
Barium „	32.9	0.4
Sodium „	27.0	0.0
Thallium „	0.5	0.04

To the two groups of chlorides which are *more* soluble in presence of hydrochloric acid (*Compt. rend.*, **91**, 986) must be added two other groups which are less soluble in solutions of the acid than in pure water. One group contains hydrated chlorides, the solubility of which is diminished by the presence of hydrochloric acid, but still remains considerable; these crystallise from acid solutions with a certain quantity of water of crystallisation. The other group includes chlorides which crystallise from both acid and aqueous solutions in the anhydrous condition, and are almost insoluble in concentrated hydrochloric acid.

C. H. B.

Combination of Sodium Oxide with Carbonic Anhydride, and Action of Sodium on Mercuric Oxide. By BÉKÉTOFF (*Bull. Soc. Chim.* [2], **34**, 327—328).—At ordinary temperatures sodium oxide is not attacked by carbonic anhydride, but at 400° combination takes place with incandescence. Taking the numbers of Thomsen, the reaction disengages 75.48 heat-units. When equivalent quantities ($\text{Na}_2 + \text{HgO}$) of sodium and mercuric oxide are heated together, only half the mercury is replaced by sodium. Half the sodium volatilises with the mercury, and a combination of the two oxides is left which is decomposed by water.

J. M. H. M.

Action of Dry Carbonic Anhydride on Quick Lime. By F. M. RAOULT (*Compt. rend.*, **92**, 189—191).—If calcium oxide in fragments of about 1 c.c., obtained by the decomposition of white marble, is placed in a flask, heated to the softening point of glass, the source of heat withdrawn, and a rapid current of carbonic anhydride passed into the flask, combination takes place with such energy that the calcium oxide becomes incandescent. The incandescence is visible in full daylight, and with 100 grams of lime will last about 15 minutes. The experiment succeeds equally well with ordinary “fat” lime, provided the latter has not been too strongly heated, and does not contain more than 2 or 3 per cent. of impurities. Whatever the variations in temperature, mass, and condition of the lime, and duration of the experiment, the amount of carbonic anhydride absorbed always corresponded with the formula $(\text{CaO})_2.\text{CO}_2$.

The *bibasic calcium carbonate* thus formed absorbs further quantities

of carbonic anhydride very slowly. Absorption is most rapid at about 550° . The continued action for 12 hours of a slow current of the gas at this temperature and under atmospheric pressure, results in the formation of a compound, $4\text{CaO} \cdot 3\text{CO}_2$. Beyond this point, direct absorption of the gas becomes extremely slow, the increase in weight at the end of a week being scarcely 1 per cent. At this rate, the formation of the normal carbonate, CaCO_3 , would require about five weeks. It would appear that Debray's statement that calcium carbonate "is destroyed and formed at the same temperature in an atmosphere of carbonic anhydride, according as the tension of this gas is less or greater than the tension of dissociation corresponding to that temperature," only holds good under certain special conditions. The calcium oxide employed in these experiments was obtained by strongly heating the nitrate.

Calcium oxide which has been heated above $1,100^{\circ}$ absorbs carbonic anhydride much more slowly than when it has only been heated to dull redness. Two samples, one of which had been heated for an hour at about $1,400^{\circ}$, whilst the other had only been heated to dull redness, were placed in a porcelain tube and heated to incipient redness in a current of dry carbonic anhydride for eight days. At the end of this time, the non-calcined specimen had absorbed an amount of the gas corresponding to the formation of $4\text{CaO} \cdot 3\text{CO}_2$, whereas the amount absorbed by the calcined specimen was only equivalent to $5\text{CaO} \cdot 2\text{C}_2\text{O}$. The same difference was observed even when the calcined lime was very finely powdered. It is apparently due to a condensation or polymerisation of the calcium oxide.

C. H. B.

Absorption-spectra of some Metals of the Yttrium and Cerium Groups. By J. L. SORET (*Compt. rend.*, **91**, 378).—*Holmium*.—This metal is characterised by a considerable number of lines and bands, more especially in the ultra-violet; three of these have hitherto been attributed to erbium. The following are some of the more characteristic:—

Ultra-red, $\lambda = 8040$; red, 6804; greenish-yellow, 5363; ultra-violet, 3680—3600, 3470—3530, and 3270.

Samarium (de Boisbaudran), *Decipium* (Delafontaine), Y_{β} (Marignac).—The spectrum of this metal (the three names probably refer to the same metal) has been already studied by de Boisbaudran as far as the violet. It gives also several bands in the violet and ultra-violet, the most characteristic being slightly less refrangible than H. and of very great intensity.

C. W. W.

Spectrum of Thulium. By R. THALÉN (*Compt. rend.*, **91**, 376).—When the absorption-spectrum given by a solution rich in thulium is compared with that of a solution of comparatively pure erbium, there are seen, besides the common bands attributable to erbium, two wide and fairly intense bands. The blacker of the two is situated between Fraunhofer's C and B ($\lambda = 6840$), in a dilute solution very near B, in a strong solution reaching almost to a; this band is not weakened by increasing the dispersive power of the spectroscope.

The second band in the blue ($\lambda = 4650$) is fairly intense, with weak dispersive power, but fades when the dispersion is strong.

The emission spectrum of thulium contains a bright band corresponding with the first of the absorption-bands, and a second bright band ($\lambda = 4760$) not corresponding with the second absorption-band.

The spark-spectrum of thulium contains a number of bright lines, of which twelve have been measured. C. W. W.

Erbium. By P. T. CLEVE (*Compt. rend.*, **91**, 381).—The author has succeeded in obtaining erbia free from all but traces of holmia and thulia.

The approximately pure earth was fractionated by decomposition of the nitrate. The first fraction gave the number 166.25 as the atomic weight of erbium, the last fraction gave 166.21—166.0. The number 166 was frequently obtained from pure erbia, and may be taken as very near the truth. Erbium oxide (erbia), Er_2O_3 , is a powder of a beautiful rose colour, which is not affected by strong heating. It dissolves in acids if not too concentrated. Its sp. gr. is 8.64. Its salts have a fine rose colour.

The *nitrate*, $\text{Er}_2(\text{NO}_3)_6 \cdot 10\text{H}_2\text{O}$, forms large crystals, unalterable in the air.

The *sulphate* crystallises with $8\text{H}_2\text{O}$, and forms a potassium and an ammonium double salt soluble in cold water.

The *selenite*, $\text{Er}_2\text{O}_3 \cdot 4\text{SeO}_2 + 5\text{H}_2\text{O}$, is precipitated by alcohol as a crystalline powder. The *oxalate* forms microscopic red crystals. The anhydrous *formate* is an indistinctly crystalline red powder; the hydrated *formate* forms fine red crystals. The *platinocyanide*, $\text{Er}_2\text{Pt}_3(\text{CN})_{12} \cdot 21\text{H}_2\text{O}$, crystallises in red prisms with violet and green reflections. The composition of the selenite and of the double sulphates with potassium and ammonium sulphate prove that erbium oxide should be represented as Er_2O_3 . C. W. W.

Gases Occluded in Aluminium and Magnesium. By DUMAS (*Compt. rend.*, **90**, 1027).—When aluminium is heated in a vacuum to the temperature at which porcelain softens, it gives off rather more than its own volume of gas, consisting mainly of hydrogen. The greater part, possibly the whole, of the gas seems to be given off suddenly at a red-white heat.

Magnesium gives off proportionately more gas, about one and a half times its own volume. 20 grams of magnesium gave 12.3 c.c. hydrogen and 4.1 c.c. carbonic oxide. Another sample (40 grams) gave 28.1 c.c. H, 1.9 c.c. CO , and 1.5 c.c. CO_2 .

During the heating of the magnesium, the metal volatilises and is deposited in the cooler parts of the vessel in brilliant crystals of the colour of silver. C. W. W.

Synthetic Production of Native Silicates of Alumina and Alkaline Silico-aluminates. By S. MEUNIER (*Compt. rend.*, **90**, 1009).—By passing the mixed vapours of silicon chloride and water over finely-divided aluminium in the right proportions, transparent needles are obtained, active to polarised light, and giving by analysis

40.91 per cent. silica and 58.02 alumina. This is the composition of andalusite and of disthene; the small dimensions of the crystals render it impossible to determine the species more exactly.

In the above experiment, if potash is added to the aluminium, brown well-defined trapezohedrons are obtained, having the composition 55.83 SiO_2 , $23.54 \text{ Al}_2\text{O}_3$, and $20.63 \text{ K}_2\text{O} = 100$. These crystals resemble amphotene in composition and crystalline form, but differ from it by their absolute neutrality to polarised light.

In addition to the above crystals, prisms resembling orthose were obtained in one experiment, but the quantity was insufficient for analysis.

By substituting soda or lime for the potash, similar results are obtained. C. W. W.

Some Ultramarine Compounds. By K. HEUMANN (*Annalen*, **203**, 174—235).—This paper is a lengthy discussion of the composition and constitution of ultramarine from analyses and manufacturing data.

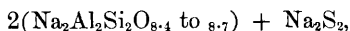
According to the author, very few trustworthy analyses of ultramarine are to be found in the literature of the substance even up to a recent date, on which a constitutional formula can be made with any certainty.

From comparison of a large number of analyses of different varieties of ultramarines by himself (*Ann.*, **199**, 253; *Ann.*, **201**, 263), Hoffman (Vien. Exhib., 1873, Report), and others, he finds the same atomic proportion to exist between the sulphur and the monatomic metal, viz., 1 : 3, and for sulphur : aluminium as 1 : 2.2 to 2.5, and for sulphur : silicon 1 : 2.4 to 2.6. Considering the difficulty of preparing a perfectly pure sample of ultramarine, it is highly probable that the atomic proportion of sulphur to aluminium and silicon is as 1 : 2 in each case, which will give to blue ultramarine the atomic constitution $\text{M}'_3\text{Al}_2\text{Si}_2\text{SO}_{8.4-8.7}$.

Starting from the fact that silver ultramarine when decomposed by acids gives up one-third of its silver as sulphide, which corresponds to almost exactly half the entire sulphur present in pure ultramarine, the author argues that this half of the total sulphur is in direct combination with the silver or sodium in the original molecule, and the remaining half in the free state or as a polysulphide, and not as has been supposed in an oxidised condition.

To prove this, ultramarine-green was blued by carefully heating in a stream of dry hydrochloric acid.

A very beautiful blue product was obtained, which gave on analysis almost exactly half the sulphur as hydric sulphide, and half in the free state, without any trace of an oxidised sulphur compound, from which it may be safely concluded that the sulphur exists in the form of a bisulphide, the formula of ultramarine-blue being probably



which may be considered as a combination of a mineral like nephelin with sodium bisulphide.

This formula for ultramarine has a close connection with that of the

members of the lazurite group of minerals, hauyn, nosean, and sodalite. As these minerals are sometimes found more or less green or blue coloured, and colourless specimens of them may be easily coloured by heating, and on treatment with acids lose their colour, evolving sulphuretted hydrogen, it was supposed by the author that they all contain some white ultramarine.

On treating powdered hauyn with gaseous hydrochloric acid, blue ultramarine was obtained, showing that these minerals are practically identical with the white ultramarine of Ritter.

The colouring substance in ultramarine is evidently a peculiarity of the form of compound or combination, and not depending on any one of the elementary bodies entering into its composition, as they are all colourless.

The subjoined table exhibits the derivation of ultramarine from alumina, and its relations to the minerals of the lazulite series.

Kaolin	$\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot\text{OH}_2$.
Nephelin	$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$.
Hauyn	$2\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot\text{Na}_2\text{SO}_4$.
White ultramarine	$2\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot\text{Na}_2\text{S}$.
Blue ultramarine	$2\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot\text{Na}_2\text{S}_2$.
Sodalite	$3\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot 2\text{NaCl}$.

W. R. H.

Formation of Permanently Green Crystals of Chromic Chloride. By A. MEUGEOT (*Compt. rend.*, 91, 389).—When hydrochloric acid acts on potassium dichromate in aqueous solution, chlorine is given off, and a dark blackish-brown solution formed which, by slow evaporation, deposits chromic chloride in large crystals of a deep violet colour, also in small green crystals. These green crystals have remained unchanged for more than two years. C. W. W.

Potassium and Ammonium Tetrachromates. By G. WYROUBOFF (*Bull. Soc. Chim.* [2], 35, 162—165).—The salts described by Darmstaedter (*ibid.*, 15, 118) as potassium nitro-dichromate and nitro-trichromate, are shown by the author to consist of potassium tetrachromate. Darmstaedter's error is caused by the fact that when nitric acid is added to potassium dichromate, large quantities of potassium nitrate separate out along with the tetrachromate, and it is very difficult to separate the two. By adding potassium dichromate to a large excess of nitric acid (sp. gr. 1.4), and allowing the clear solution to stand, crystals of potassium tetrachromate separate out. It may also be obtained in a similar manner from the trichromate. The trichromate is obtained by adding potassium dichromate to nitric acid of sp. gr. 1.24.

The author has prepared potassium and ammonium tetrachromates, both of which contain traces of nitric acid retained in minute cavities in the crystals; this accounts for the nitrous fumes obtained by Darmstaedter on heating his preparations. L. T. O'S.

Preparation of Crystallised Chromates. By L. BOURGEOIS (*Jahrb. f. Min.*, 1880, 1, Ref. 351).—The strontium and calcium salts

are prepared in the same manner as the barium salt (this Journal, **36**, 437), viz., by heating the corresponding chlorides (2 mols.) with a mixture of potassium chromate (1 mol.) and sodium chromate (1 mol.) to bright redness.

The *strontium salt* forms beautiful yellow lamellæ, cleaving parallel to the faces of a rhombic prism of $161^{\circ} 40'$, and exhibiting the optical characters of the rhombic system. It is sparingly soluble in water, and is decomposed by prolonged exposure to a red heat.

The *calcium salt* crystallises in slender yellow needles, formed from a rectangular prism; these dissolve readily in water, and decompose at a red heat more quickly than the strontium salt.

The isomorphous mixtures of barium and strontium chromate, and of barium and calcium chromate, each in molecular proportions, have the aspect of barium chromate. The corresponding chromate of strontium and calcium crystallises like strontium chromate.

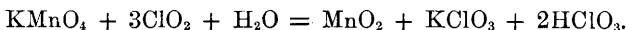
The author regards the sulphates and chromates of the alkaline earth-metals as geometrically and chemically isomorphous.

H. W.

Artificial Formation of Pyrolusite. By J. B. HANNAY (*Min. Mag.*, 1878, No. 9, 967; *Jahrb. f. Min.*, 1880, **1**, Ref. 351).—On adding a few granules of potassium chlorate to a warm solution of manganous nitrate, the whole of the manganese is precipitated in flat tablets, having a splendid purple tint when very thin, and red when thicker. The appearance of these crystals varies according to the temperature at which they are formed and the strength of the acid; with very strong acid, at about 20° , the small tablets separate out after a few days in radial tufts, exhibiting under the microscope exactly the appearance of native pyrolusite. Sp. gr. = 4.935. If an iron salt is present, part of it is precipitated in the form of a double manganate of manganese and iron.

H. W.

Action of Chlorine Tetroxide on Potassium Permanganate. By E. FÜRST (*Annalen*, **206**, 75—78).—The action takes place in accordance with the formula:



O. H.

Two Furnace-products. By W. C. BRÖGGER (*Zeitschr. f. Kryst.*, 1879, **3**, 492).—1. *Crystals of an Alloy of Lead and Silver from Kongsberg.*—This alloy, containing about 27 per cent. silver, was found in beautiful crystals on the sole of a smelting furnace in Kongsberg. The crystals were partly octohedrons, joined together in various ways so as to form rods and plates; partly long six-sided prisms, apparently made up of rhombic dodecahedrons, elongated in the direction of a trigonal intermediate axis.

2. *Crystals of a compound of sulphur with copper and iron from Röras*, containing 31.64 per cent. Cu, 34.16 Fe, and 34.79 S (= 100.59), and therefore agreeing approximately with the formula $4\text{CuS}, 5\text{FeS}$, or with $2(\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3), \text{FeS}$. The compound appears therefore to belong to the series of variegated copper ores, and may perhaps be placed between cuban and erubescite. Crystals of the octohedron,

mostly combined with the cube, occur both as distinct individuals, and as twins united by an octohedral face. Cleavage, octohedral, imperfect. $H. = 4$; sp. gr. 3.97. Easily fusible; colour, dark greenish-yellow to pinchbeck-brown, with variegated tarnish. H. W.

Silver Sulphate. By P. BRAHAM (*Chem. News*, **42**, 163).—Sulphate of silver was prepared in the form of brilliant transparent crystals of high refractive power, by pouring on a plate of pure silver strong sulphuric acid, and adding a few drops of strong nitric acid. At first there was a slight action. In a day or two the whole of the acid acquired a deep purple tint, and after the lapse of two or three weeks, the purple tint sinks towards the silver, and a slight brown tint can be seen on the surface. The layer above the silver being colourless about this period, large crystals form, which redissolve, and the liquid becomes colourless. In the course of a few days brilliant specks are seen, which develop into perfect crystals of a regular octohedral shape. The author has in his possession crystals which have taken over six months in growing. D. B.

Recrystallisation of Argentiferous Bismuth. By C. WINKLER (*J. pr. Chem.* [2], **23**, 298—302).—The author confirms Schneider's statement (*J. pr. Chem.* [2], **23**, 75) that silver may be extracted from argentiferous bismuth, by a process analogous to Pattinson's method for desilverising lead. On recrystallising 150 kilos. of bismuth containing 0.101 per cent. of silver, 21.8 per cent. of the total silver was found in the bismuth crystals, and 78.2 per cent. of the silver in the molten residue. It is, however, doubtful whether the process will ever have any practical value. W. C. W.

Action of Chlorine on Inorganic Silver Salts. By J. KRUTWIG (*Ber.*, **14**, 304—307).—This investigation is a continuation of the observations made by Spring (*Bull. de l'Acad. Roy. de Belg.* [2nd series], 39 and 46), that chlorine acts on silver chlorate, forming silver chloride and chlorine trioxide, and on silver nitrite, forming silver chloride and nitroxyl chloride.

Chlorine acts on *silver bromate* at 50° , forming chlorine monobromide and silver chloride and oxygen. This action is explained by the supposed formation of ClO_3Br , which decomposes into oxygen and chlorine bromide. The action of chlorine on *silver iodate* is analogous to the above, but requires a higher temperature, and the iodine monochloride formed combines with chlorine, yielding iodine trichloride.

Chlorine acts on *silver sulphite* at the ordinary temperature, sulphurous anhydride, oxygen, and silver chloride being formed. Sulphuric dichloride, SO_2Cl_2 , is in all probability a result of the action, since potassium sulphate is formed in the caustic potash used to absorb the gases. The action of chlorine on *silver sulphate* is indirect, and only takes place when the salt has been fused and decomposed by the heat.

Chlorine acts on *silver chromate* at temperatures above 200° , silver chloride, chromic anhydride, and oxygen being formed. The action of chlorine on *silver selenite* is analogous to its action on the sulphite;

silver chloride, selenious anhydride, and oxygen are formed. It is without action on silver selenate or silver molybdate, even when fused. The reaction with silver permanganate is very energetic; oxygen is evolved, and a residue of silver chloride and manganese dioxide being obtained.

P. P. B.

Compounds of Hydrochloric Acid with Mercuric Chloride.

By A. DITTE (*Compt. rend.*, **92**, 353—355).—When a solution of mercuric chloride in hydrochloric acid is cooled to about -10° , and saturated with hydrochloric acid gas, brilliant colourless transparent crystals are obtained, of the composition $\text{HgCl}_2 \cdot 2\text{HCl} \cdot 7\text{H}_2\text{O}$, which melt at about -2° , with decomposition.

If a stronger solution of mercuric chloride is saturated with the acid gas at about 5° , and the liquid if necessary cooled slowly to 0° , large distinct crystals of the compound $3\text{HgCl}_2 \cdot 4\text{HCl} \cdot 14\text{H}_2\text{O}$ separate out. This compound crystallises in short, thick, colourless, transparent prisms, decomposes when exposed to the air, and melts on slight elevation of temperature. When the solution of the mercuric chloride is of such strength that crystals are deposited at about 15° , one obtains, according to the concentration of the solution, either large, elongated, transparent, colourless prisms, or smaller needles of the same form. They have the composition $2\text{HgCl}_2 \cdot \text{HCl} \cdot 6\text{H}_2\text{O}$, decompose when exposed to the air, becoming white and opaque, and at a slightly elevated temperature they melt, lose hydrochloric acid and water, and leave a residue of mercuric chloride. If the solution is saturated with acid at temperatures between 15° and 40° , long brilliant silky prisms of the composition $4\text{HgCl}_2 \cdot 2\text{HCl} \cdot 9\text{H}_2\text{O}$ are deposited. This compound behaves exactly like the preceding one. When the mercuric chloride solution is saturated with the acid gas at 80 — 90° , and allowed to crystallise at about 60° , it deposits long silky white needles, resembling asbestos, and having the composition $3\text{HgCl}_2 \cdot \text{HCl} \cdot 5\text{H}_2\text{O}$. If the solution crystallises at higher temperatures, white nacreous plates are obtained, which contain the same proportion of mercuric chloride and acid as the preceding compound, but appear to be anhydrous. They are, however, very difficult to isolate.

From these experiments, it follows that solutions of mercuric chloride in hydrochloric acid will contain free mercuric chloride, free hydrochloric acid, and one, two, or more of the above hydrochlorides in proportions depending on the degree of concentration of the acid and on the temperature.

C. H. B.

Analysis of a Crystalline Mercury Salt. By P. BRAHAM (*Chem. News*, **42**, 163).—This salt was prepared by the action of sulphuric acid with a trace of nitric acid on metallic mercury in the cold. The operation whereby these crystals were produced extended over two years, the resulting crystals being in the form of rhombic prisms, and remaining transparent only as long as they were covered with the most concentrated sulphuric acid. An instant's exposure to the air, or exposure for a few hours under the acid, changed them into an amorphous white, highly deliquescent powder. Owing to the crystals

absorbing water with great rapidity, it became almost impossible to be certain of the real weight of a sample. A quantitative determination of the acid made by boiling a weighed amount with solution of carbonate of sodium, and precipitating as barium sulphate, gave results which showed that the salt is a mercurous sulphate; further analyses with the salt, whilst still unchanged under the acid in which it was formed, gave numbers agreeing with the formula HgHSO_4 . The excess of SO_3 (3 per cent.) found arises from the difficulty of weighing without absorption of water, and the difficulty of perfectly freeing the salt from sulphuric acid without decomposing it. D. B.

Mineralogical Chemistry.

Variability of the Angles of Crystals. By F. PFAFF (*Jahrb. f. Min.*, 1880, **1**, Ref. 152).—The author has made a series of measurements to determine how far even well-developed crystals with specular surfaces exhibit deviations from the law of “invariability of the dihedral angles.” The angles measured were such as could be calculated from the symmetry of the system, independently of the influence of the lengths of the axes. The results showed that the variations from the calculated values were not insignificant, amounting in some cases to nearly half a degree. The author regards these anomalies, not as a surface phenomenon, but as a consequence of disturbances of the structure of the crystals, the frequent occurrence of which is corroborated by optical anomalies, and he comes to the conclusion that the limits of admissible correction of measured angles by calculation from rational axial sections must be carried further than has hitherto been the case.

The measurements were made by daylight, by means of a diminishing telescope. The results are given in the following table:—

Mineral.	Measured angle.	Deviation from the calculated angle in minutes.		
		Mean.	Max.	Min.
Garnet from the Mussa Alp ..	$\infty O : \infty O$	$13\frac{3}{4}$	15	13
Fluorspar from Stolberg	$\infty O \infty : \infty O \infty$	$9\frac{1}{2}$	11	7
Zincblende: cleavage specimen	$\infty O : \infty O$	$10\frac{1}{2}$	11	10
Iron pyrites from Traversella .	$O : O$	27	29	26
	$\infty O 2 : \infty O 2$	$20\frac{1}{2}$	21	19
“ “ “ “ “	$\frac{2}{2} : \frac{2}{2}$			
Zircon	$\infty P : \infty P$	11	13	$9\frac{1}{2}$
Vesuvian, brown	$\infty P : \infty P \infty$	$10\frac{1}{4}$	12	8
Beryl	$\infty P : \infty P$	6	7	5

The angles of 120° and 90° were found to be exact to $1'$, in a beryl, an emerald, a green vesuvian, and in rock crystal from Marmarosch and from the Wallis. H. W.

Colours of the Diamond in Polarised Light. By E. JANNETTAZ (*Jahrb. f. Min.*, 1880, 1, Ref. 157).—A diamond (probably from the Cape) cut in the tabular form parallel to an octohedral face, was found by the author to exhibit very brilliant colours in polarised light. These colours were not due to any peculiar condition of the surface of the stone, which indeed exhibited all the characters of the regular system, but are regarded by the author as probably arising from the presence of an enclosed crystal. Such an enclosure would produce a tension in its immediate neighbourhood, and cause the diamond at certain parts of its surface to act on polarised light. In accordance with this view, H. Michel-Lévy adduces the enclosures of iron-glance, H. Damour that of topaz in diamond; the last-named enclosures are regarded by Fizeau as capable of producing the appearances described by Jannettaz. C. Klein mentions a similar observation made by Schrauf (*Mon. Mitth.*, 1873, 289), to the effect that a yellowish diamond intergrown with a white one gave rise to abnormal optical phenomena. H. W.

A New Variety of Native Carbon, being the Highest Known Member of the Series of Amorphous Carbons. By A. INOSTRANZEFF (*Jahrb. f. Min.*, 1880, 1, Memoirs 97—124).—This coal, closely allied to anthracite, is found near Schunga, on the western shore of Lake Onega, where the principal formations consist of black clay-slates interrupted by greenstones. The coals of this formation may be divided into four groups, viz. :—

1. A pure black coal, which has an adamantine-metallic lustre, easily scratches Iceland spar, and gives less easily with fluorspar a black slightly lustrous streak, so that its hardness is between $3\frac{1}{2}$ and 4. It splits in two directions, perpendicular to the surface of the seam and to each other, and in a third direction perpendicular to the other two and parallel to the surface of the seam. It is traversed by numerous fissures, which are filled with quartz, calcspar, and ferric oxide. Dilute hydrochloric acid dissolves the two latter, leaving the quartz-veins pure and transparent, and the coal with a stronger and more truly adamantine lustre, which however becomes dull after repeated handling.

2. To the second group belongs a coal having a higher specific gravity than the first, in consequence of containing a much larger proportion of ash. It is black, with prismatic cleavage and faint graphitic lustre. Many lumps appear tarnished on the surface, and are mostly coated with ferric oxide, sometimes with a thin crust of quartz. Here and there may be observed fine veins of iron pyrites. The fractured surface of this variety is slightly conchoidal, and mostly exhibits a stronger graphitic lustre than the natural surface. Many lumps contain fibres of white asbestos 3 mm. thick, sometimes forming several parallel layers. The streak-colour of this variety is between black-grey and grey-black.

3. A third group consists of an earthy variety formerly known as "Olonez earth." It is mostly black, sometimes blackish-grey, and very soft, but hardens on exposure to the air. It has a higher specific gravity than either of the preceding types, on account of its larger proportion of ash.

4. To the fourth group belongs a mineral sent to the author as anthracite, but really consisting of a black clay-slate; some varieties of it resemble lydite. It has generally a very homogeneous aspect and slightly conchoidal fracture; streak-colour grey.

All these coals contain water. The black shining variety (group 1) when heated to 100—120° gives off its water very slowly. On heating it in a water-bath it lost 2.03 per cent. of water in 71 days, and when it was subsequently heated for 32 days longer at 120° in an air-bath the total loss amounted to 3.93 per cent. All the varieties are difficult to burn, and for analysis it was necessary to burn them in a stream of oxygen in a tube filled partly with copper oxide, partly with lead chromate.

Analyses.—I. Black coal with diamond lustre. Ash, dark brown, consisting of 0.48 per cent. ferric oxide and 0.51 silica.

II, III, IV, V. Coals of the second group. II. Lustre graphitic. Ash of lighter reddish-brown colour. III. Coal with spotty tarnish. Ash light brick-red. IV. Coal with similar external aspect and graphitic lustre. Ash reddish-grey. V. Black, slightly staining coal, having a graphitic lustre on the newly fractured surface. Ash ochrey-grey.

VI, VII, VIII. Earthy varieties belonging to group 3. VI and VIII. "Black Olonez earth;" VI, black; VIII, blackish-grey; ash light ochrey-grey. VII is a mass of coal and clay artificially prepared by the action of dilute hydrochloric acid on dark grey dolomite.

IX and X. Varieties belonging to the fourth group, *i.e.*, clay-slates coloured by carbonaceous matter. IX is a black slightly staining substance, yielding a light-grey ash; X, a black siliceous slate, nearly allied to lydite, and yielding a white ash.

	C.	H.	N.	S.	H ₂ O.	Ash.	Total.	Sp. gr.
I.	90.50	0.40	0.41	—	7.76	1.01 =	100.08	1.841
II.	69.74	0.21	—	0.12	5.89	23.95 =	99.91	1.931
III.	66.84	0.25	—	1.34	5.94	25.81 =	100.18	2.035
IV.	63.57	0.39	—	0.73	5.42	29.77 =	99.88	1.978
V.	59.43	0.29	—	2.22	5.40	32.17 =	99.51	2.117
VI.	35.39	0.14	—	0.43	4.56	59.60 =	100.12	2.348
VII.	25.50	0.12	—	—	3.55	76.77 =	99.94	—
VIII.	18.19	0.16	—	0.44	3.44	77.92 =	100.15	2.527
IX.	15.56	0.12	—	0.50	1.38	82.32 =	99.88	2.572
X.	4.5	0.02	—	—	0.40	95.7 =	100.09	2.603

The chemical composition of the Olonez coal shows distinctly that it is the most highly carbonised member of the series of amorphous carbons or coals, and this composition agrees with its structure and physical properties, *e.g.*, its density, hardness, adamantine lustre, elec-

tric conductivity, and specific heat (0.1922 according to the author's experiments). In this series, it stands nearest to anthracite, which has hitherto been regarded as the highest member of the series. In its proportion of carbon it is equal to the best graphites from Ceylon. It is not, however, a true graphite, inasmuch as when oxidised with a mixture of nitric and sulphuric acids, or with potassium chlorate and nitric acid, it does not yield either graphitic acid or Brodie's graphite, but behaves like an amorphous coal. H. W.

Occurrence of Anthracite in an Iron Mine in Norberg, Sweden. By G. NORDENSTRÖM (*Jahrb. f. Min.*, 1, 1880, Ref. 158).—This black, glassy, lustrous, non-staining coal was raised from the depth of about 20 meters in the small Kallmora mine in north-east Norberg. It originates from a black ore mixed with chlorite and hornblende, and bounded immediately by eurite. The coal contains iron pyrites, and is partly coated by chlorite, which also lines numerous narrow clefts in it. Sp. gr. = 1.53; hardness = 2.5. Infusible; burns very slowly. Quite free from ulmic acid. An analysis of the coal by C. G. Dahlerus gave:—

Non-combustible gases	6.4
Combustible gases	14.5
Carbon	66.0
Dark, reddish-grey ash	13.1

Small pieces of anthracite are indeed of frequent occurrence in the primitive mountain range of Sweden, the only peculiarity of the specimen above mentioned being its size (500 c.c.). H. W.

New Resin from Köflach, in Styria. By C. DÖLTER (*Jahrb. f. Min.*, 1880, 2, Ref. 152).—This resin has the empirical composition $C_{29}H_{43}O_2$, melts at about 98°, has a density of 1.2 to 1.25, is soluble in ether and carbon sulphide, insoluble in alcohol, aqueous or anhydrous, and in potash-ley. Strong nitric acid converts it, with intumescence, into a brown viscid mass. When fused with potash it carbonises, and emits a not unpleasant odour.

Other chemically similar resins from the same locality are: two modifications of *Jaulingite* (Zepharovich), soluble in alcohol and in ether; three varieties of an unnamed resin described by Rumpf, all soluble in alcohol; and, lastly, four resins belonging to the retinite group, viz., *Pyroretin*, *Reussinite*, *Leucopetrite*, and *Euosmite*.

H. W.

Minerals of the Sarrabus Mine, Sardinia. By A. RICHARD (*Jahrb. f. Min.* 1880, 1, Ref. 333).—The lead and silver mining district of Sarrabus in Sardinia yields from three veins, Monte Narba, Giovanni Bono, and Bacca Arroddas, a large number of minerals. The matrix consists of calcite, fluorspar, heavy spar, quartz, and steatite (heavy spar is not found in Monte Narba), and the rocks which inclose these minerals are designated as granitic porphyries, hornblende-quartzite with magnetic pyrites, and black shales with iron pyrites and veins of calcite.

The minerals which occur together are native silver, silver-glance,

psaturose, red silver ore, galena, blende, copper pyrites, fahl-ore, wulfenite, cerussite, breithauptite, harmotome, gypsum, dolomite, arragonite. H. W.

Chemical Analysis of Hungarian Fahl-ores. By K. HIDEGH (*Jahrb. f. Min.*, 1880, 1, Ref. 334).—The following table exhibits the composition of a number of these ores:—

	Kapnik : crystallised.	Kapnik : massive; shining.	Szászka : crystallised.	Nagjág : crystallised.	Herzengrund : crystallised.
Sulphur...	25·31	24·25	25·98	26·52	25·75
Arsenic...	2·88	1·08	19·11	12·07	4·75
Antimony.	24·21	25·63	0·10	11·35	22·82
Silver	1·32	6·76	0·08	0·29	0·05
Copper...	37·83	32·59	53·60	39·75	39·81
Iron	0·94	0·90	0·39	1·77	4·75
Zinc.....	7·25	5·77	—	5·55	1·44
Manganese	traces	0·83	traces	1·23	—
Sp. gr...	99·74 4·91	97·81 4·885	99·26 4·92	98·53 4·61	99·37 4·77

The calculation of the amount of sulphur on the assumption that the sulphides of the several metals have the formulæ As_2S_3 , Sb_2S_3 , Cu_2S , Ag_2S , FeS , ZnS , MnS , agrees very well with the values actually found. With the general formula $(\text{As, Sb})_2 \text{S}_7 \text{M}$, in which M denotes the quantity of each of the several metals which is equivalent to 1 atom of silver, the analyses do not agree quite so well. The cause of the difference may perhaps be sought in the want of uniformity of the material. H. W.

Christophite from St. Agnes, Cornwall. By J. H. COLLINS (*Mineralogical Magazine*, 1879, 91).—This mineral occurs either massive, granular, and of dark brown colour, or less frequently in black shining crystals. Its general characters are those of an ordinary dark blende, but by careful manipulation a button of zinc may be reduced from it. The mean of several analyses of the granular mineral gave—

Zn.	Fe.	Sn.	S.	Al_2O_3 .	SiO_2 .	CuCaO .
32·0	22·4	1·3	29·5	7·2	6·8	traces = 99·2

whence the composition of the pure mineral may probably be calculated as follows:—

Zn.	Fe.	Sn.	S.	ZnS.	FeS.	SnS.	S.
37·6	26·2	1·4	34·7	= 99·9,	or 56·1	41·1	1·9 0·8 = 99·9

The presence of tin is remarkable, but from the solubility of the mineral in *aqua regia*, the author infers that the tin is an essential constituent, and that it is present as stannic sulphide. The mineral

is therefore very nearly related to Breithaupt's christophite, but contains, besides the tin, a considerably larger proportion of iron sulphide.

The crystals, which resemble the dolomite crystals from the Binnenthal, form combinations of the cube with the two tetrahedrons, nearly in equilibrium. One of the tetrahedrons is smooth and shining, the other uniformly dull. The cube-faces are deeply striated parallel to the combination-edge with the smooth tetrahedron, which character is exactly opposite to that of the Binnenthal blende. Dodecahedral cleavage perfect.

H. W.

Chemical Composition of Guanajuatite. By J. W. MAILLET (*Jahrb. f. Min.*, 1880, **1**, Ref. 160).—An analysis of this mineral mixed with a small portion of matrix gave—

Se.	S.	Bi.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	H ₂ O.
31·64	0·61	59·92	2·53	traces	3·47	1·46 = 99·63;

whence may be deduced:—

	Guanajuatite	92·17
Matrix {	Halloysite	6·72
	Silica	0·56
	Hygroscopic water	0·18
		<hr/> 99·63

Pyrite could not be detected.

The composition of guanajuatite reckoned to 100 parts is—

Se.	S.	Bi.
34·38	0·66	65·01

leading to the atomic proportion Bi : (Se + S) = 310 : 453, and to the formula Bi₂Se₃.

H. W.

American Sulpho-selenides of Mercury. By G. J. BRUSH and W. J. COMSTOCK (*Sill. Jour.* [3], **21**, 312).—*Onofrite*.—Found in limestone at Marysville, Southern Utah, in small fragments, showing no trace of crystalline form. Colour and streak, blackish-grey; fracture conchoidal, with brilliant metallic lustre on fresh surfaces. Hardness about 2·5; sp. gr. 7·62. When heated, the greater part volatilises, giving reactions for sulphur, selenium, and mercury. With borax, it forms an amethystine bead. Composition—

Se.	S.	Hg.	Zn.	Mn.
4·58	11·68	81·93	0·54	0·69 = 99·42

which may essentially be represented as Hg(S,Se)

The compositions of the American sulpho-selenides of mercury now known are given in the following table:—

	S.	Se.	Hg.	Zn.	Mn.	Fe.	Quartz.
Metacinnabarite..	13·82	—	85·79	—	—	0·39	0·25
Guadalcazarite ..	14·01	tr.	83·90	2·09	—	—	—
„ ..	14·58	1·08	79·73	4·23	—	tr.	—
Onofrite, Utah ..	11·68	4·58	81·93	0·54	0·69	—	—
„ San Ono-							
fre	10·30	6·49	81·33	—	—	—	—
Tiemannite.....	0·70	23·61	74·02	—	—	—	—

C. W. W.

Mineralogical Notices. By A. WEISBACH (*Jahrb. f. Min.*, 1880, 2, Mem. 109—114).—1. *Hypargyrite*.—The author has already pointed out (*Zeitschr. f. Kryst.*, 2, 63) that Breithaupt's hypargyrite from Andreasberg agrees in its morphological and physical characters, as well as in qualitative chemical composition, with miargyrite, and further that it contains the same proportion of silver as the latter, viz., 36·02 per cent. The complete identity of the two minerals is established by the following analyses of so-called hypargyrite:—

Ag.	Sb.	As.	S.
37·74	41·02	undet.	21·20 = 99·96
37·06	41·13	0·79	21·50 = 100·48

The formula of miargyrite, AgSbS_2 , requires 36·74 per cent. silver, 41·49 antimony, and 21·77 sulphur.

2. *Lepidophæite* from Kamsdorf in Thuringia is a reddish-brown mineral with faint silky lustre, and somewhat shining streak; it has about the hardness of talc, and therefore leaves a stain when rubbed. Specific gravity, apparently very small, even less than 1, on account of enclosed air, which cannot be completely expelled except by prolonged heating under water; real sp. gr. = 2·89—3·04. The mineral blackens when heated in a tube, and dissolves in hydrochloric acid with evolution of chlorine, forming a dark-brown liquid, which afterwards turns light yellow. Analysis gave 58·77 per cent. MnO_2 , 9·59 MnO , 11·48 CuO , and 21·05 water, leading to the formula $\text{CuMn}_6\text{O}_{12} + 9\text{H}_2\text{O}$. The considerable amount of copper which the mineral contains shows that it cannot be regarded as a variety of wad. Qualitatively indeed it is more nearly allied to the cupreous manganese of the same locality, from which, however, it differs essentially by its crystalline character.

3. *Uranotil*.—This egg-yellow uranic silicate occurs, together with zeunerite, walpurgin, &c., in the “Weisser Hirsch” mine at Neustadt, not only in capillary crystals and pilose nodules, but also in thick masses having a radiofibrous fracture. Analysis of two very pure specimens gave—

CaO .	U_2O_3 .	Fe_2O_3 .	SiO_2 .	H_2O .
5·13	63·93	3·03	13·02	14·55 = 99·66
5·49	62·84	2·88	14·48	13·79 = 99·48

The iron contained small quantities of aluminium and cobalt. Regarding the ferric oxide as taking the place of part of the uranic oxide, these numbers lead to the formula given by Boricky for Bavarian

uranotil, viz., $\text{CaU}_6\text{Si}_3\text{O}_{16} + 9\text{H}_2\text{O}$, or $\text{CaO} \cdot 3\text{U}_2\text{O}_3 \cdot 3\text{SiO}_2 + 9\text{H}_2\text{O}$, which requires 4·44 per cent. CaO , 68·46 U_2O_3 , 14·26 SiO_2 , and 12·84 H_2O .

4. *Bismuthite*.—This mineral, first recognised as a distinct species by Breithaupt, and constituting, next to native bismuth, the most abundant and widely diffused of all bismuth-ores, has hitherto been analysed only qualitatively.

The following quantitative analysis was made upon a specimen from a mine at Neüstädte, having a weak fatty lustre, a light-grey colour, and small conchoidal fracture, occurring in the pseudomorphs after acute rhombohedral bismuth-crystals (-2R) imbedded in quartz—after it had been completely freed by levigation from quartz and remains of native bismuth. It gave 95·90 per cent. Bi_2O_3 ; 2·91 CO_2 , and 1·04 water, leading to the formula $3\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$, which requires 95·77 Bi_2O_3 , 3·00 CO_2 , and 1·23 H_2O .

In thin section bismuthite appears transparent, greyish-yellow, and double-refracting: it is therefore not amorphous as Breithaupt was inclined to suppose.

Identical with bismuthite in chemical composition and specific gravity, are the small grey and brown concentrically stratified nodules lately found in the Wolfgang-Maassen Mine at Neustadt-Schneeberg.

5. *Cacochlor* (Lithiophorite).—In former analyses of this mineral from Bergersdorf, near Görlitz, the water was determined by loss, and it was left doubtful whether the silica belonged to the compound or was merely mechanically mixed.

A new analysis was therefore made, which gave—

MnO.	O.	CoO.*	CuO.	Bi_2O_3 .	Al_2O_3 †	CaO and BaO.
50·95	9·50	4·31	0·55	0·41	11·46	0·73
		K_2O and Li_2O .	SiO_2 .	H_2O .		
		1·25	3·88	16·59	= 99·63	

As the separated silica does not dissolve in sodium carbonate, it is probably only mixed. On this hypothesis, the composition of the mineral may be approximately represented by the empirical formula, $\text{AlMn}_2\text{O}_7 + 4\text{H}_2\text{O}$, which requires 56·61 per cent. MnO , 13·56 Al_2O_3 , 29·76 O , and 19·13 water.

6. *Leucite*.—This mineral from the Alban Mountains has been only once analysed, namely, by Klaproth in 1797. The following analyses of transparent yellowish-white crystals, having a specific gravity of 2·179 at 10° , from the lava of the Colli Cimini, were made at the author's instigation by Dr. H. Schulze :—

SiO_2 .	Al_2O_3 .	K_2O .	Na_2O .
54·91	22·85	21·48	0·41 = 99·65

The alumina contained a trace of ferric oxide. Neither calcium nor lithium was present.

H. W.

* With NiO .

† With Fe_2O_3 .

Telluric Silver from Batés in Transylvania. By J. A. KRENNER (*Jahrb. f. Min.*, 1880, 2, Ref. 26).—This mineral, found in a vein of ore occurring in mica-slate, consists of four silver tellurides. Some of the crystals are shining and of a light grey colour; others are coated with a blackish sooty crust. They belong to the regular system, and exhibit the faces $\infty O\infty$, ∞O , O , $2O$, $\infty O2$, $\infty O3$, and subordinate $2O2$. Their aspect is either cubic, or prismatic and cauliform. Among the accompanying minerals are small black quartz-crystals, brown-red zinc-blende, iron pyrites, and copper pyrites (sometimes decomposed and of green colour), and a few crystals of adularia. Many of the silver telluride crystals, when freed from the crust above mentioned, appear as if sprinkled with gold-dust. H. W.

The Crystal System of Manganite. By A. SADEBECK (*Jahrb. f. Min.*, 1880, 1, Ref. 332).—The author agrees with Groth in regarding this mineral as holohedro-rhombic. This view is supported:—1. By the rarity of the occurrence of hemihedral forms, which when they appear separately, must be regarded as merely accidental modes of development. 2. By the furcate formation due to the parallel arrangement of the individual crystals, and having nothing in common with twin-formation. 3. The non-occurrence of any difference of physical conformation on the pyramidal faces. 4. The absence of any different forms in the two positions, such as is exhibited by crystals having a hemihedral development.

The reasons for regarding the *diamond* as holohedral are, according to the author, exactly similar to those above adduced, so that to be consistent, both those minerals must be regarded either as holohedral or as hemihedral. H. W.

Bastnäsite and Tysonite from Colorado. By O. D. ALLEN and W. J. COMSTOCK (*Sill. Jour.* [3], 19, 390).—*Bastnäsite*.—Hardness, 4–4·5; sp. gr., 5·18–5·20; colour, reddish-brown; but slightly soluble in hydrochloric acid, decomposed by strong sulphuric acid with evolution of carbonic acid and hydrofluoric acid. Composition—

(Ce,La,Di) ₂ O ₃ .	(Ca,La,Di).	CO ₂ .	F (by diff.).
50·13	21·82	20·15	7·90 = 100·00

corresponding with the formula $R_2F_6 + 2R_2(CO_3)_3$.

Tysonite.—Occurs with bastnäsite from Pike's Peak, Colorado, in worn, indistinct crystals, probably prismatic, exhibiting distinct cleavage; hardness, 4·5–5; sp. gr. = 6·14; colour, pale wax-yellow. Composition—

Ce.	La,Di.	F (by diff.).
40·19	30·37	29·44 = 100

corresponding with the formula $(Ce,La,Di)_2F_6$. From the mode of occurrence of these two minerals, it is probable that bastnäsite is formed by the change of the fluoride (tysonite) into fluocarbonate.

C. W. W.

Analyses of some Apatites containing Manganese. By S. L. PENFIELD (*Sill. Jour.* [3], 19, 367).—These minerals occur at Branch-

ville, Conn., U.S., either in crystalline masses imbedded in felspar or in more or less distinct crystals; the colour varies from dark-green, almost black, to white. Analysis I is of the darkest specimen found; II is a somewhat lighter specimen; III is the analysis of the white variety; and IV is of a crystallised variety from Franklin Furnace, New Jersey, occurring in calcite, from which it can readily be separated.

	I.	II.	III.	IV.
P ₂ O ₅	41·63	40·96	41·47	39·59
Al ₂ O ₃	—	0·50	—	0·56
Fe ₂ O ₃	0·77	0·08	0·22	0·77
CaO	40·31	47·87	49·12	46·64
MnO	10·59	2·48	1·96	1·35
ZnO	—	—	—	0·03
Ca.....	3·29	4·04	2·88	3·57
F	3·12	3·84	2·68	3·37
Cl.....	0·03	—	0·10	0·04
CaCO ₃	—	—	—	2·82
H ₂ O	—	—	—	0·52
Insoluble	—	0·06	1·50	—
	99·74	99·83	99·93	99·26
Sp. gr.....	3·39	—	3·144	3·22

C. W. W.

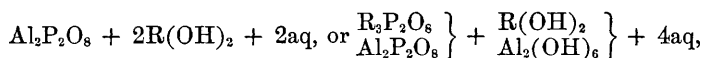
Chemical Composition of Childrenite. By S. L. PENFIELD (*Sill. Jour.* [3], 19, 315).—With the view of showing the relationship of childrenite to eosphorite (Brush and Dana, *Sill. Jour.*, July, 1878), a careful analysis of a pure specimen of childrenite was made with special attention to the discovery of alkalis and ferric oxide. The results of two analyses are here given:—

	P ₂ O ₅ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	H ₂ O.	Quartz.
I.	30·19	21·17	26·54	4·87	1·21	15·87	0·10 = 99·95
II.	29·98	21·44	26·20	—	—	—	—

No alkalis and no ferric oxide were found. The ratio given by these numbers is—

$$\text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3 : \text{RO} : \text{H}_2\text{O} = 1 : 1 : 2 : 4 \quad (\text{R} = \text{Fe, Mn, Ca}),$$

corresponding to the empirical formula $\text{R}_2\text{Al}_2\text{P}_2\text{O}_{10} \cdot 4\text{H}_2\text{O}$, which may be written—



which is the same as the formula made out for eosphorite.

C. W. W.

Relation between Childrenite and Eosphorite. By G. J. BRUSH and E. S. DANA (*Sill. Jour.* [3], 19, 316).—Childrenite and eosphorite are crystallographically closely homeomorphous, the axial ratios being—

	c. (Vert.)	b. (Macrodiag.)	a. (Brachydiag.)
Childrenite	0·667	1·294	1·000
Eosphorite	0·663	1·287	1·000

The relation of the two minerals in composition is seen from the analysis of childrenite by Penfield (*see above*). The formulæ of the two minerals are identical, the difference being that while childrenite contains chiefly iron (26·54 FeO, 4·87 MnO), eosporite contains chiefly manganese (7·4 FeO, 23·51 MnO). C. W. W.

Hopeite. By DAMOUR and DES CLOIZEAUX; also by FRIEDEL and SARASIN (*Jahrb. f. Min.*, 1880, 2, Ref. 24—26).—This mineral was described by Brewster in 1824, and has been chemically examined by Nordenskiöld, but its constitution has hitherto not been clearly made out. It was supposed to be a hydrated zinc phosphate, but its great rarity gave no opportunity for re-examination. Lately, however, Damour has examined it chemically and found it to contain phosphoric acid and zinc with a small quantity of iron; and Des Cloizeaux has found that it belongs to the orthorhombic system, exhibiting the forms $\infty P\infty$, $P\infty$, P , $\infty P\infty$, $\infty P\frac{1}{2}$, with $\frac{1}{3}P\infty$ and $0P$ subordinate. According to Levy, the forms ∞P and $\infty P\frac{3}{2}$ likewise occur. Fundamental angles $\infty P\infty : \infty P\infty$ over $P = 140^\circ$; $P : P\infty = 129^\circ 30'$. Axial ratio $a : b : c = 0·57221 : 1 : 0·47169$. The plane of the optic axes, as observed by Brewster, is parallel to the base; the first median line is negative and perpendicular to the lateral pinacoid. Axial dispersion slight; $\rho < v$. Apparent angle of axes in air (larger than that given by Brewster) $2E = 78^\circ 3'$ (red glass), $78^\circ 35'$ (sodium flame).

Friedel and Sarasin have prepared hopeite artificially by heating equal weights of zinc oxide and phosphoric anhydride with water in a sealed tube at 150 — 180° for sixteen hours. In this manner, rhombic crystals were obtained exhibiting either the faces $\infty P\infty$, ∞P , $0P$, or the combination $\frac{1}{3}P\infty . \infty P\infty$. These crystals agreed with those of natural hopeite in the magnitudes of their angles and in their optical characters, and gave by chemical analysis 31·42 p. c. P_2O_5 , 53·52 ZnO, and 14·45 H_2O , agreeing nearly with the formula $Zn_3P_2O_8 + 4H_2O$, or $3ZnO, P_2O_5 + 4H_2O$, which requires 31·07 P_2O_5 , 53·18 ZnO, and 15·75 H_2O . H. W.

Kjerulfin. By M. BAUER (*Jahrb. f. Min.*, 1880, 1, Mem. 75—78).—This mineral, first analysed by von Kobell, was regarded by him as a distinct species. Bauer, however, in 1875 pointed out that von Kobell's analysis was incorrect, giving too much fluorine—a statement confirmed by Rammelsberg (*Mineralchemie*, 2 Aufl., 697)—and further suggested that kjerulfin might be identical with wagnerite, or rather a wagnerite more or less decomposed, a view which has been confirmed by later researches.

The analyses which have been made of kjerulfin are given in the following table: the differences show that some of them were made with material more or less altered:

Phosphoric acid	42.22	44.23	42.35	43.7	43.83
Magnesia	37.00	44.47	46.01	46.0	49.33
Lime	7.56	6.60	4.81	3.1	—
Soda, with a little potash ..	1.56	—	1.54	—	—
Insoluble matter	1.50	—	2.04	0.9	—
Alumina and ferric oxide ..	5.40	—	0.65	—	—
Fluorine	4.78	6.23	5.06	10.7	11.73
Loss by ignition	—	0.77	—	—	—
	100.02	102.30	102.46	104.4	104.94

I is v. Kobell's first analysis, which led to the formula $2\text{Mg}_3\text{P}_2\text{O}_8, \text{MgF}_2$ (neglecting Ca and Na); II is Rammelsberg's, who deduced from it the formula $2\text{Mg}_3\text{P}_2\text{O}_8, \text{MgO}, \text{MgF}_2$. Analysis III was made at the author's instigation by Friederici with yellow material having a fatty lustre and an appearance of freshness, with no perceptible impurities, and a specific gravity of 3.10. The fluorine was carefully determined by the method of Fresenius. Analysis IV was made by Pisani (this Journal, 36, 441), who examined the homogeneous glassy-lustrous interior of large crystals, which, as appears by comparison with the composition of normal wagnerite given under V, is perfectly identical with the latter.

All these results confirm the identity of fresh unaltered kjerulfin with wagnerite. Kjerulfin is, however, for the most part much decomposed, the magnesia being more or less replaced by lime, and the mineral thereby gradually converted into apatite, as shown especially in the crystals examined by Pisani, the fresh yellow mass of which is traversed by more or less opaque white veins, which are rich in lime, and consist of a mixture of kjerulfin and apatite, whilst the entire crust—and frequently also the nucleus—is almost wholly converted into apatite, so that these large kjerulfin crystals are on the way of forming pseudomorphs of apatite after wagnerite; a complete pseudomorphosis has, however, not yet been observed.

Kjerulfin occurs, together with large masses of apatite, in the apatite strata of Havredal, Oedegarden, &c., in Norway, whence it is probable that the entire mass of apatite there occurring has been formed by transformation of pre-existing wagnerite. H. W.

Artificial Libethenite. By C. FRIEDEL and E. SARASIN (*Jahrb. f. Min.*, 1880, 2, Ref. 153).—The cupric phosphate which occurs native as libethenite is very easily produced artificially. Debray (*Ann. Chim. Phys.* [3] 61, 439) states that it is formed on heating $\text{P}_2\text{O}_5, 3\text{CuO}, \text{H}_2\text{O}$ with water in sealed tubes; also, in presence of cupric sulphate and nitrate, when the solution is heated to 100° , and in presence of cupric chloride at 200° . Other mixtures from which Friedel and Sarasin obtained various arsenates of copper, or of copper and sodium, likewise yielded libethenite in the form of a whitish-green crystalline powder, as soon as phosphoric acid was added to them, and the resulting precipitate was boiled. Very fine crystals of libethenite, measuring 1 mm. on the longitudinal edges, were obtained with excess of phosphoric acid in sealed tubes at 181° . These crystals

exhibited the forms ∞P and $P\infty$, and agreed with native libethenite in the magnitude of their angles.

Libethenite, prepared by either of the methods above described, exhibits a reaction which may serve very well to distinguish it from olivenite. On heating it in the state of powder to redness out of contact with reducing gases, it gives off water, turns brown, and, on cooling, assumes a fine green colour. If the heat is not raised high enough, the colour remains brownish, even after cooling; if, on the contrary, the heat be too strong, even though not high enough to fuse the powder, the substance will assume a grey tint and lose its lustre. Olivenite when ignited yields only a brown powder. H. W.

Phosphorised Copper-ores. By A. SCHRAUF (*Zeitschr. f. Krystall.* [4], 1, 33; *Jahrb. f. Min.*, 1879, 336—340).—1. The *Lunnite Group*.—This group includes the minerals *phosphorochalcite*, $\text{Cu}_5\text{P}_2\text{H}_6\text{O}_{14}$; *ehlite*, $\text{Cu}_5\text{P}_2\text{H}_6\text{O}_{13}$; and *dihydrite*, $\text{Cu}_5\text{P}_2\text{H}_4\text{O}_{12}$. The crystallised varieties are commonly spoken of as dihydrite; the amorphous as pseudomalachite.

The *lunnites*, as formerly determined by Tschermak, are triclinic. The amorphous varieties are binary or ternary mixtures, in various proportions, of phosphorochalcite, ehlite, and dihydrite. They are kidney-shaped, with concentrically scaly structure, have a density of 4.2, and experience a perceptible loss of weight at 200° . Different from these are the soft, light grey-green, radio-fibrous specimens from Ehl ($H = 2$; sp. gr. 4.10), which are decomposed dihydrites, and contain silicate of copper; to these the vulgar name *ehlite* may be assigned. The crystallised varieties consist mainly of dihydrite; they have the relatively smallest amount of water; the highest sp. gr. = 4.4; and do not sustain any loss of weight at 200° .

2. *Libethenite*.—This mineral was formerly supposed to be rhombic, but more exact measurements have shown it to be monoclinic; $a : b : c = 1.4255 : 1.134625 : \beta = 90^\circ 56'$. Observed faces $\infty P\infty$, $\infty P\infty$, $0P$, ∞P , $-P$, $+P$, $-P\infty$, $+P\infty$, $+\frac{1}{3}P\infty$.

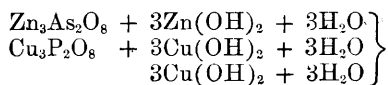
3. *Thrombolite* was described by Breithaupt and Plattner as a hydrated copper phosphate. The author, however, finds, by a new analysis of the mineral (under the microscope, yellow-green, homogeneous, apolar; sp. gr. 3.6681) that it does not contain phosphoric acid, but is rather a cupric antimonite. Analysis gave:—

Loss by ignition (H_2O)	=	16.56	
CuO	=	39.44	
Fe_2O_3	=	1.05	
Sb_2O_5 (from Sb_2O_4)	=	6.65	} $\text{Sb}_2\text{O}_3 + \text{Sb}_2\text{O}_5 = 42.95$
Sb_2O_3 (from Sb_2S_3)	=	32.52	
Total loss (Sb_2O_3 ?)	=	3.78	
<hr/>			
100			

These numbers agree most nearly with the combination of the molecules $10\text{CuO} + 3\text{Sb}_2\text{O}_3 + 19\text{H}_2\text{O}$. On account of the homogeneity of the substance, it is probably a true cupric antimonite, and not a mere mixture of cupric and antimonious oxides.

4. *Veselyite* from Moravicza in the Bannat; thin crusts on garnet-rock, or its decomposition-product, brown iron ore. Since the establishment of this species by the author in 1874 (this Journal, **28**, 546), he has been enabled to complete his earlier observations by the examination of good fresh material. Colour and streak greenish-grey. $H. = 3.5-4$; sp. gr., 3.351. Triclinic, $a : b : c = 0.7101 : 1 : 0.9134$; $\alpha = 89^\circ 31'$; $\beta = 103^\circ 50'$; $\gamma = 89^\circ 34'$. Observed faces: $\infty P\infty$, $\infty P\infty$, $0P$, $\infty P'$, ∞/P , $P'\infty$, $P'\infty$, $2P\tilde{2}$, $2P\infty$. Crystals simple, apparently monoclinic. Their shape is determined by the predominant prism ∞P in combination with the brachydome $P\infty$; the pyramid $2P\tilde{2}$ is rare; the transverse dome $2P\infty$ has been observed only once. The angles $\infty P' : \infty/P$ and $P'\infty : P'\infty$ are nearly identical in magnitude with the corresponding angles in libethenite; and angles of nearly the same magnitude occur in the zinc arsenate called *adamin*. The great inclination of the edges $\infty P' | \infty/P : P'\infty | P'\infty$ ($103^\circ 50'$) affords, however, a characteristic difference between the forms of veselyite and libethenite.

Analysis gave 37.34 CuO, 25.20 ZnO, 9.01 P_2O_5 , 10.41 As_2O_5 , and 17.05 H_2O , leading to the empirical formula $9CuO, 6ZnO, P_2O_5, As_2O_5, 18H_2O$. The simple rational formula, $4CuO, P_2O_5 + 5H_2O$ must therefore be replaced by the following:—



H. W.

Sulphates occurring on the Bauersberg, near Bischofsheim, in front of the Rhongebirge. By S. SINGER (*Jahrb. f. Min.*, 1880, **2**, Ref. 151).—On the uneven surface of the basalt of the Bauersberg, there has been deposited a bed of pyritiferous lignite, which is completely surrounded by the basalt, while its upper layers frequently alternate with basaltic tufa. The decomposition of the pyrites in this formation has given rise to a considerable number of sulphates, not forming sharply-defined layers, but often combined in such a manner that they separate together in concentric shells or spherical concretions, and enclose or interpenetrate one another. The surface of this layer of sulphates at the border of the basaltic tufa and lignite is, according to Hilger's investigation, covered with keramolite, whilst the layer itself, in addition to two bodies not exactly determinable, contains the following salts:—

1. *Reddish-white Alum* = $RSO_4, R_2(SO_4)_3 + 24H_2O$, wherein $RO = FeO$ and CoO , and $R_2O_3 = Al_2O_3$ and Fe_2O_3 . Sp. gr. 1.594 at 12° . Melts before the blowpipe in its water of crystallisation, with strong intumescence. Easily soluble in water, the solution on boiling depositing a red-brown precipitate not containing sulphuric acid. Optical character that of the regular system.

2. *Plagiocitrite* (Sandberger) = $R_2SO_4, R_2SO_6 + 9H_2O$, with $R_2O = K_2O, Na_2O, FeO, MgO, CaO, NiO, CoO$ and $R_2O_3 = Al_2O_3$ with Fe_2O_3 .—Sp. gr. 1.881 at 13° . Colour lemon-yellow. Melts before the blowpipe in its water of crystallisation, with strong intumescence, leaving a red-brown spongy residue. Easily soluble in water, the solution when

boiled depositing ferric oxide free from sulphuric acid. The small crystals appear to be triclinic, exhibiting the base, prism, and lateral pinacoids; but it is also possible to regard them as monoclinic.

3. *Clinophrite* (Sandberger), $5R_2SO_4 + R_2O_3 \cdot 3H_2O + 5Aq$ with $R_2O = K_2O, Na_2O, FeO, MgO, CaO, NiO$, and $R_2O_3 = Fe_2O_3$ with Al_2O_3 . Sp. gr. = 2.979 at 12°. Blackish-green; powder grey-green. Melts with intumescence before the blowpipe, and, when strongly ignited, leaves a magnetic residue. Sparingly soluble in water; solution deposits ferric oxide on boiling. The crystals are probably monoclinic: $\infty P, 0P, P\infty$; angle $\infty P : \infty P = 85^\circ$.

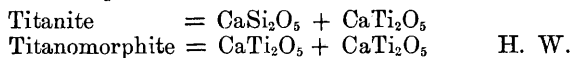
4. *Wattevillite* (Singer) = $RSO_4 + 2H_2O$, with $R = Ca, Na, K, Mg, Co, Ni, Fe$.—Sp. gr. = 1.81 at 13°. Snow-white; swells up before the blowpipe, and fuses with some difficulty to a white tumefied enamel. Dissolves very easily in cold water; the solution, when heated or left to evaporate, depositing crystals of gypsum. Crystallises in large needles, probably rhombic or monoclinic. In polarised light, distinct multiple combinations may be recognised.

H. W.

Rutile in Gastaldite-Eclogite from Val Tournanche. By A. COSSA (*Jahrb. f. Min.*, 1880, Mem. 162).—This rock derives its name from its principal constituent, a blue mineral which has been shown by the author to be identical with the gastaldite discovered in 1875 by Strüver at Brozzo in the Val d'Aosta (*Rammelsberg's Mineralchemie*, 2 Aufl., 682). A microscopical examination of a thin section of the rock revealed the presence of irregularly scattered yellowish-brown double-refracting crystals, which, in polarised light, exhibited the characters of a quadratic mineral. These crystals, at first mistaken for zircon, were found by chemical analysis to consist of rutile. The analysis was made by digesting about 40 grams of the pulverised rock for 48 hours on the water-bath with dilute hydrofluoric acid; evaporating the solution to dryness; decomposing the residual fluorides with dilute sulphuric acid; digesting the resulting whitish-grey powder with hydrochloric acid; then washing it carefully, and repeatedly lixiviating it with a solution of potassio-mercuric iodide. This process readily yielded a sufficient quantity of a yellow-brown powder, which, on microscopical examination, was found to consist of the small crystals above mentioned. They had the form of the knee-shaped twin-crystals of rutile, and exhibited the following properties:—1. They are not decolorised even at a very high temperature. 2. With phosphorus salt on charcoal and in the reducing flame, they easily give the violet coloration characteristic of titanium. 3. They are completely decomposed by fusion with hydropotassic sulphate, and the acid solution, after dilution and prolonged boiling, yields a precipitate of titanous acid. 4. With excess of ammonia the cold acid solution yields a white precipitate, which dissolves completely in hydrochloric acid, yielding a solution which colours turmeric paper brown. 5. The hydrochloric acid solution, heated with tin, yields the violet colour characteristic of titanium compounds, and after reduction, does not colour turmeric paper brown, which must have been the case if the substance under examination had contained zirconia. 6. On expelling the greater part of the free acid from the hydrochloric acid

solution, then adding ammonium oxalate in excess, afterwards ammonium carbonate, and filtering from the resulting titanium precipitate, not a trace of zirconia could be detected in the filtrate. These reactions are regarded by the author as affording satisfactory evidence that the small crystals above mentioned, as occurring in gastaldite-eclogite, consist of rutile. H. W.

Titanomorphite, a new Calcium Titanate. By A. v. LASAULX (*Zeitschr. f. Krystallographie*, 1879, 162; *Jahrb. f. Min.*, 1880, 2, Ref. 142).—This is a white mineral, with a faint greenish tinge, which occurs, accompanying rutile, in a garnet-amphibolite of the "hohe Eule" between Reichenbach and Neurode in Silesia. It has the composition $\text{CaO}, 2\text{TiO}_2$, and forms monoclinic crystals exhibiting the faces ∞P , P , 0P , $\frac{1}{2}\text{P}\infty$, $\text{P}\infty$, $+\frac{2}{3}\text{P}2$. Apparent angle of the optic axes in air about $45-50^\circ$. Axial dispersion strong, $\rho > \nu$. The optical and chemical, as well as the crystallographic characters, indicate isomorphism between titanomorphite and titanate:—



Constitution of the Pyroxene Group. By C. DÖLTER (*Jahrb. f. Min.*, 1880, 2, Ref. 289).—In this paper the author gives a summary of the results which he has obtained in the chemical examination of the individual members of this group, including, (1), a survey of the chemical constitution of the several varieties; (2), of the constitution of the individual pyroxene-silicates; (3), of the relations between the crystallographic constants and the chemical constitution of the individual pyroxenes; (4), some remarks on their physical properties and molecular volumes; and (5), a classification of the pyroxenes.

1. *Special Chemical Composition of the Several Varieties.*

(1.) **RHOMBIC PYROXENES.**—Enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$ (or in simplest expression, MgSiO_3).

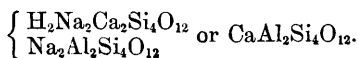
Bronzite, $\left\{ \begin{array}{c} \text{Mg}_2\text{Si}_2\text{O}_6 \\ \text{Fe}_2\text{Si}_2\text{O}_6 \end{array} \right\}$, in varying proportions, together with a small quantity of $\text{CaMgSi}_2\text{O}_6$ (sometimes none); $\text{MgAl}_2\text{SiO}_6$, often in not inconsiderable proportion; $\text{MgFe}_2\text{SiO}_6$ always in very small quantity; Mn as $\text{MnCaSi}_2\text{O}_6$ and $\text{Mn}_2\text{Si}_2\text{O}_6$, also in very small quantity.

Hypersthene, all containing R_2O_3 , like aluminiferous augite:—

$\left. \begin{array}{l} \text{Mg}_2\text{Si}_2\text{O}_6 \\ \text{Fe}_2\text{Si}_2\text{O}_6 \end{array} \right\}$ with $\left. \begin{array}{l} \text{MgAl}_2\text{SiO}_6 \\ \text{MgFe}_2\text{SiO}_6 \end{array} \right\}$ from 2 to 15 p. c.; a small quantity of $\text{CaMgSi}_2\text{O}_6$ and $\text{CaMnSi}_2\text{O}_6$.

Hypersthene is therefore related to bronzite in the same manner as augite to diopside.

(2.) **MONOCLINIC PYROXENES.**—Wollastonite, CaSiO_3 .—Pectolite, crystallographically isomorphous with the pyroxenes. It is certainly a decomposed mineral, and its formula may be deduced from $\text{CaNaSi}_2\text{O}_6$ by assumption of water. A small quantity of Al_2O_3 is always present.



By the presence of sodium, these two very closely-related minerals are brought very near to the alkali-pyroxenes.

Diopside, $\text{CaMgSi}_2\text{O}_6$ (70–90 p. c.)	} in small quantities.	$\text{CaFe}_2\text{Si}_4\text{O}_{12}$, rare; always
$\text{CaFeSi}_2\text{O}_6$ (30–10 p. c.)		in small quantities.
$\text{MgAl}_2\text{SiO}_6$		CaSiO_3 , appears to be
$\text{MgFe}_2\text{SiO}_6$		altogether wanting.
$\text{MnCaSi}_2\text{O}_6$		

Chrome-diopside is a diopside contaminated with picotite and chrome-iron ore.

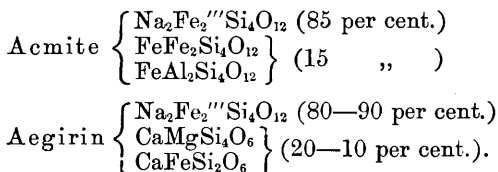
Hedenbergite, $\text{CaFeSi}_2\text{O}_6$, with small quantities of $\text{CaMgSi}_2\text{O}_6$, $\text{CaMnSi}_2\text{O}_6$, and a silicate of sesquioxide.

Schefferite is probably $\left. \begin{array}{l} \text{CaMnSi}_2\text{O}_6 \\ \text{CaMgSi}_2\text{O}_6 \end{array} \right\}$, with small quantities of $\text{FeCaSi}_2\text{O}_6$, $\text{MgFe}_2\text{Si}_2\text{O}_6$, and perhaps $\text{Mg}(\text{Mn}_2)^{\text{vi}}\text{Si}_2\text{O}_6$.

Jeffersonite, $\left. \begin{array}{l} \text{CaMnSi}_2\text{O}_6 \\ \text{CaFeSi}_2\text{O}_6 \end{array} \right\}$, predominant, with smaller quantities of $\text{CaZnSi}_2\text{O}_6$, $\text{CaMgSi}_2\text{O}_6$, $\text{Mn}_2\text{Si}_2\text{O}_6$, $\text{Zn}_2\text{Si}_2\text{O}_6$, and traces of aluminium silicate.

Aluminiferous Augite, $\text{CaMgSi}_2\text{O}_6$, predominant (generally more than half), together with $\text{CaFeSi}_2\text{O}_6$ (5–25 per cent.), and $\left. \begin{array}{l} \text{MgAl}_2\text{SiO}_6 \\ \text{MgFe}_2\text{SiO}_6 \end{array} \right\}$ 10–25 per cent., and finally small quantities of $\text{Mg}_2\text{Si}_2\text{O}_6$, $\text{Fe}_2\text{Si}_2\text{O}_6$, $\text{CaMnSi}_2\text{O}_6$, with traces of $\text{Na}_2\text{R}'''_2\text{Si}_4\text{O}_{12}$ and $\text{CaFe}''_2\text{Si}_4\text{O}_{12}$, in some cases; also CaSiO_3 . The proportion of the silicates of monoxides to the silicates of sesquioxides varies between 60 : 1 and 3 : 1.

Diallage.—Difficult to determine, on account of decomposition and the want of iron-determinations. Some varieties contain sesquioxides; others do not. They contain either $\text{MgCaSi}_2\text{O}_6$, with much $\text{FeCaSi}_2\text{O}_6$, either alone or together with $\text{MgAl}_2\text{SiO}_6$, perhaps also $\text{FeAl}_2\text{SiO}_6$, often in considerable quantities, and small quantities of the corresponding ferric silicates. Diallages are therefore chemically undistinguishable from the diopsides and the aluminiferous augites—



Acmite and aegirin are probably for the most part identical.

Spodumene, $\left\{ \begin{array}{l} \text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12} \text{ (60–70 per cent.)} \\ \text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \text{ (20–10 per cent.)} \end{array} \right\}$, with small quantities of $\text{CaMgSi}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$; perhaps also of petalite, $\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12}$.

Petalite, probably isomorphous with spodumene; isomorphous mixtures not exactly determinable on account of analytical difficulties.

Petalite is probably $\left\{ \begin{array}{l} \text{Li}_2\text{Al}_2\text{Si}_{10}\text{O}_{24} \text{ (80–90 per cent.)} \\ \text{Na}_4\text{Al}_4\text{Si}_8\text{O}_{24} \text{ (20–10 per cent.)} \end{array} \right\}$, with traces of

$\text{CaMgSi}_2\text{O}_6$, $\text{CaFeSi}_2\text{O}_6$, and probably small quantities of spodumene silicate.

(3.) TRICLINIC PYROXENES.— $\left. \begin{array}{l} \text{Rhodonite, Mn}_2\text{Si}_2\text{O}_6 \\ \text{Pajsbergite, CaMnSi}_2\text{O}_6 \end{array} \right\}$, in various proportions, sometimes with $\text{CaFeSi}_2\text{O}_6$ and small quantities of $\text{CaMgSi}_2\text{O}_6$.

Bustamite, $\left\{ \begin{array}{l} \text{CaMnSi}_2\text{O}_6, \text{ frequently predominant, and} \\ \text{Mn}_2\text{Si}_2\text{O}_6. \end{array} \right.$

Fowlerite, $\left\{ \begin{array}{l} \text{Mn}_2\text{Si}_2\text{O}_6 \text{ predominant} \\ \text{Fe}_2\text{Si}_2\text{O}_6 \\ \text{CaMgSi}_2\text{O}_6 \\ \text{CaZnSi}_2\text{O}_6 \end{array} \right\}$ or perhaps $\left\{ \begin{array}{l} \text{MnSi}_2\text{O}_6 \\ \text{Fe}_2\text{Si}_2\text{O}_6 \\ \text{CaMgSi}_2\text{O}_6. \\ \text{CaMnSi}_2\text{O}_6 \\ \text{Zn}_2\text{Si}_2\text{O}_6 \end{array} \right.$

Babingtonite.—The analyses are not very concordant, so that the calculation is somewhat hypothetical. I. Babingtonite from Arendal, according to Rammelsberg's analysis. II. From Herborn-seelback, according to Jehn's analysis—

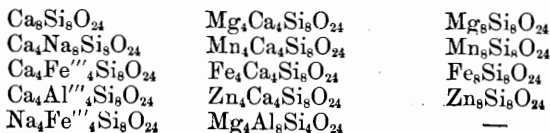


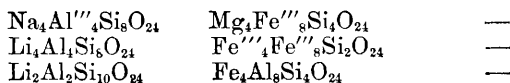
Szaboite.—Formula not determinable, for want of an iron-determination.

(2.) *The Constituent Silicates of the Pyroxene Group.*—In the following table the constituent silicates of augite are enumerated, first in their simplest form; secondly, on the assumption that, on account of their probable isomorphism with petalite, they should be referred to the general form, $\text{R}''_2\text{Si}_8\text{O}_{24}$.

	I.		II.
$\text{R}''\text{SiO}_3$.	Enstatite, wollastonite.		$\text{R}''_8\text{Si}_8\text{O}_{24}$. Diopside, &c.
$\text{R}''_2\text{Si}_2\text{O}_6$.	Diopside, hedenbergite, rhodonite.		$\text{R}''_4\text{R}''''_8\text{Si}_4\text{O}_{24}$. Aluminiferous augite.
$\text{R}''\text{R}''''_2\text{SiO}_6$.	Aluminiferous augite.		$\text{R}''_2\text{R}''''_4\text{Si}_8\text{O}_{24}$. Babingtonite.
$\text{R}'_2\text{R}''''_2\text{Si}_4\text{O}_{12}$.	Alkali-augite.		$\text{R}'_8\text{R}''''_4\text{Si}_8\text{O}_{24}$. Pectolite.
$\text{R}''\text{R}''''_2\text{Si}_4\text{O}_{12}$.	Babingtonite, and the rare silicates probably isomorphous with it.		$\text{R}'_4\text{R}''''_4\text{Si}_8\text{O}_{24}$. Alkali-augite.
$\text{R}'_2\text{R}''''_2\text{Si}_{10}\text{O}_{24}$.	Petalite.		$\text{R}'_2\text{R}''''_2\text{Si}_{10}\text{O}_{24}$. Petalite.
$\text{R}'_4\text{R}''''_2\text{Si}_4\text{O}_{12}$.	Pectolite.		

Substituting for R' , &c., the symbols of the corresponding metals, we obtain the formula of the following compounds, of which those distinguished by a star occur alone, while the others only in mixtures:—





If petalite be supposed not to belong to the group, all these formulæ may be reduced to $\text{R}''_4\text{Si}_4\text{O}_{12}$. Mixed pyroxenes contain for the most part only members of one and the same series; I and III appear to be altogether immiscible, but mixtures occur containing I and II, or II and III.

(3.) *Molecular Volumes*.—Referring the above-mentioned silicates to the general formula $\text{R}''_8\text{Si}_8\text{O}_{24}$, their relative volumes may be represented by the following numbers, with the reservation that the specific gravities are somewhat uncertain:—

Enstatite.....	8	Wollastonite	10
Diopside.....	8	Aegirin	8
Hedenbergite..	8·8	Spodumene	7·7
Rhodonite	8·8	Petalite	9·5
Pectolite	10.		

(4.) *Physical Properties*.—Those members of the group which are more or less removed from the rest in a chemical point of view, viz., wollastonite, pectolite, and petalite, likewise differ from the rest in their facility of cleavage and in their optical properties.

(5.) *Relations between the Angular Magnitudes of the Crystals and their Chemical Composition*.—The results obtained with regard to these relations being somewhat undecided, a reference to them here must suffice.

(6.) CLASSIFICATION OF PYROXENES.

Augites containing both Mono- and Sesqui-oxides.

	Rhombic.	Monoclinic.	Triclinic.
Magnesium aluminium augite..	Hypersthene	—	—
Calcium aluminium augite	—	{ Al-augite. Diallage, in part.	—
Calcio-ferric augite	—		Babingtonite.

Augites containing only Monoxides.

Magnesium augite	Enstatite.	—	—
Iron augite	Bronzite.	—	—
Calcium augite	—	Wollastonite.	—
Manganese augite	—	—	Rhodonite.
Calcium iron augite	—	Hedenbergite.	—
Calcium magnesium augite	—	{ Diopside. Diallage, in pt.	—
Calcium manganese augite	—		Pajsbergite.
Calcium zinc augite	—	Schefferite.	Bustamite.
		Jeffersonite.	Fowlerite.

Alkali Augites.

	Rhombic.	Monoclinic.	Triclinic.
Sodium potassium augite	—	Pectolite.	—
Sodium iron augite	—	Acmite (Aegirin).	—
Lithium aluminium augite	—	Spodumene.	—
Lithium aluminium silicon augite	—	Petalite.	—

H. W.

Barsowite. By M. BAUER (*Jahrb. f. Min.*, **1**, Mem. 63-75).—This rock, the matrix of the Uralian corundum and spinell, has hitherto been found only in the form of boulders in the gold-fields of Barsowkoi near Kyschtinsk, south of Katherinenburg in the Ural, and was first described by Gustav Rose (*Pogg. Ann.*, **48**, 367), who regarded it as a distinct mineral species. Des Cloizeaux, Dana, Geuth, and others looked upon it, on the other hand, as a mineral allied to amorphite, or as a variety of that species, and Quenstedt regarded it as allied to scapolite. The result of Bauer's investigation is to confirm the statement of Rose that barsowite is a distinct mineral species, and further that it has the composition of anorthite, but differs from that mineral in its crystalline form and other physical properties.

Barsowite, as it occurs in nature, is intimately mixed with calcite and corundum. To analyse it, an estimation of carbonic acid was first made in order to determine the quantity of calcite present. The finely powdered mineral was then decomposed by hot hydrochloric acid, the gelatinous silica thereby separated remaining mixed with the insoluble corundum, while the remainder of the substance passed into solution. The dissolved portion was then analysed separately, and the silica was extracted from the insoluble residue by solution of sodium carbonate, the substance then remaining undissolved consisting of pure alumina, being in fact the corundum mixed in small granules with the barsowite. The results of three analyses thus made are given in the following table:—

	Corundum.	SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O, Na ₂ O.
I..	7.56	38.57	34.27	18.54	—	1.06*
II..	14.74	35.78	30.81	16.81	0.28	1.58*
III..	16.90	33.81	30.19	16.28	—	2.82*

Deducting the corundum, we obtain the values below:—

	SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Alkalis.	
I'..	41.72	37.07	20.05	1.16		= 100
II'..	42.20	36.35	19.82	0.33	1.30	= 100
III'..	46.69	36.33	19.59	3.39		= 100

* Determined by difference.

These numbers, especially those in II', agree nearly with the composition of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, viz., 43.08 per cent. SiO_2 , 36.82 Al_2O_3 , and 20.10 CaO .

Barsowite and anorthite must therefore be regarded as heteromorphous states of the same chemical compound, inasmuch as they differ in crystalline form, anorthite being triclinic, whereas barsowite is rhombic, or perhaps monoclinic; also in their sp. gr. and chemical behaviour. The sp. gr. of pure barsowite, after correction for the admixed corundum, is 2.584, whereas that of anorthite is 2.67 to 2.76, mean 2.72.

With regard to the chemical behaviour of the two minerals, barsowite, as already observed, is easily decomposed by hydrochloric acid, with separation of gelatinous silica. With the aid of heat and with the mineral in fine powder, the decomposition is almost instantaneous, and the whole suddenly solidifies to a thick tenacious jelly. The behaviour of anorthite is totally different, varying indeed in different specimens, but never approaching the extraordinarily easy decomposibility of barsowite; moreover, the silica is never separated as a perfect jelly, but always either in pulverulent or in gummy form, and the mass after the decomposition never becomes quite solid.

The minerals intergrown with barsowite in the crude rock are: a light yellowish mica in thin laminæ, corundum, and spinell. The corundum occurs either in small greyish granules scattered through the entire mass, or in larger, distinctly crystallised, very acute dihexahedrons with sharp edges and summits. These distinct crystals are sometimes of a more or less dark blue colour, sometimes transparent and colourless, sometimes spotted with blue, and are found only on particular lumps of barsowite, but these mostly aggregated in large numbers, frequently even exceeding in quantity the pure barsowite itself.

The spinell is a dark green ceylonite crystallised in acute octohedrons of various sizes up to that of a pea, and pretty uniformly distributed through the entire mass of the barsowite. According to an analysis by Abich, it consists of 66.95 per cent. alumina, 18.93 magnesia, and 14.33 ferrous oxide. Friederici, on the other hand, found it to contain ferrous oxide and alumina, with only traces of lime, magnesia, and silica. Hence it would appear that these spinell-granules are not all of the same composition. The pure ferrous aluminate, $\text{FeO}, \text{Al}_2\text{O}_3$, mentioned by Abich does not appear to have been previously observed. An isomorphous mixture of it with noble spinell, $\text{MgO}, \text{Al}_2\text{O}_3$, would form the mineral called *Ceylonite*.
H. W.

Note on a Chromiferous Garnet found on the Pic Posetz, near the Maladetta (Pyrenees). By A. DAMOUR (*Jahrb. f. Min.*, 1880, 1, Ref. 170).—From this locality, a mountainous forest tract, the author obtained a pale-green crystalline rock, consisting of limestone, quartz, garnet, and a whitish mass easily fusible before the blowpipe (perhaps wernerite or zoisite).

On dissolving the lime-stone in nitric acid, small druses come to light containing garnet in rhombic dodecahedrons. The crystals are split in various directions, and therefore easily pulverised. Hard-

ness = 6.7. Sp. gr. = 3.43. Before the blowpipe, this garnet melts to a black non-magnetic glass, and yields an emerald-green enamel with fluxes.

Analyses.—From Pic Posetz, by Damour; from Orford in Canada, by Sterry Hunt:—

Pic Posetz.					
		Oxygen-ratio.			Orford.
Silica	36.20	—	19.30	2	36.65
Alumina	10.20	4.75	9.67	1	17.50
Chromic oxide	6.50	2.04			6.20
Ferric oxide	9.60	2.88	9.79	1	—
Ferrous oxide	8.16	1.81			4.97
Manganous oxide	0.50	0.13			—
Lime	27.50	7.85			33.20
Magnesia	—				0.81
Volatile constituents.	—				0.30
	98.66				99.63

The mineral from Pic Posetz may accordingly be represented by the formula $3(\text{CaO}, \text{FeO}, \text{MnO}) + (\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Cr}_2\text{O}_3) + 3\text{SiO}_2$. On account of the small amount of chromium in these minerals, they cannot be regarded as uwarowite, but are intermediate between uwarowite, almandin, and melanite.

H. W.

Nephrite and Bowerite from New Zealand. By F. BERWERTH (*Jahrb. f. Min.*, 1880, 1, Ref. 170).—In a large block of nephrite from New Zealand weighing 128.32 kilos., the author observed a number of small prisms 5 mm. long, irregularly imbedded in the compact nephrite. These crystals were cleavable parallel to the prismatic faces, and likewise exhibited hollow forms indicating hornblende-prisms with narrow truncation of the acute prismatic edge. Measurements of two small cleavage-specimens agreed pretty accurately with actinolite, with which also the colour and lustre were in accordance. Microscopical examination showed the surfaces of separation obliquely inclined to the prismatic axis, exactly as in the actinolite which occurs intergrown in mica- and chlorite-slates. Sp. gr. 3.0895.

Analysis of these transparent crystalline particles gave:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.
56.55	0.21	6.21	13.60	19.78	2.81 = 99.16

The fresh appearance of these crystals indicates that the water in them is combined. The formula deducible from this analysis, as also from that by Rammelsberg of actinolite from Arendal, is—



The compact nephrite in which these crystals were imbedded, exhibited nothing essentially new on microscopic examination. It gave by analysis:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.
57·35	0·22	5·94	13·47	20·70	3·13 = 100·81

leading to the formula $\text{Si}_{20}\text{Fe}_2\text{Ca}_5\text{Mg}_{11}\text{H}_8\text{O}_{62}$.

Both analyses negative the presence of a normal silicate, and point to an excess of silicic acid and to the presence of water, the amount of which stands to the excess of silica in the ratio 2 : 3 in the first, and 1 : 2 in the second. The compact nephrite mass contains therefore 1 mol. water more than the crystals. H. W.

Pyrophyllite from Schuylkill Co., Pennsylvania. By F. A. GENTH (*Jahrb. f. Min.*, 1880, 1, Ref. 344).—This mineral, occurring in the carboniferous shales of "North Mahony Colliery" (Old Silliman Colliery), near Mahony City, Pa., was formerly mistaken for damourite, but its true nature was first demonstrated by the author's analysis. It is found in thin horizontal veins in the "Back Mountain" seam, mostly parallel to the coal-seams, less frequently in either directions, and as a petrifying agent of the coals there occurring. It has not hitherto been found in any other situation. The veins are finely fibrous, and in lustre and general aspect have a strong resemblance to chrysotil; the fibrous structure may be seen under the microscope even in layers of the thickness of paper. Thicker veins sometimes enclose a thin layer of pyrites, the crystals of which are imprinted on the pyrophyllite. The fibrous pyrophyllite, as well as the pyrites, is sometimes covered with a layer of a scaly, silver-white mineral (not analysed) having the thickness of paper, and a silky lustre. The thickest vein observed of the fibrous pyrophyllite had a thickness of 9 mm.

The pure pyrophyllite is white to yellowish-white, with a silky to nacreous lustre, and very soft. Sp. gr. = 2·804. (According to Websky the sp. gr. of pyrophyllite varies from 2·78 to 2·92.) Infusible before the blowpipe, but exhibits the exfoliation which is characteristic of pyrophyllite. Not decomposed by acids. Its analysis gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	H ₂ O.
66·61	27·63	0·16	0·10	5·43 = 99·93

leading to the formula of pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{11} + \text{H}_2\text{O}$, which requires 66·52 SiO₂, 28·49 Al₂O₃, and 4·99 H₂O.

The above-mentioned occurrence of pyrophyllite is interesting, as the first known instance of this mineral playing the part of a petrifying agent; whereas Gümbel has shown that the petrifying agent of certain graptolites is different in composition from pyrophyllite, and that the same is the case with the petrifying agent of the coal-plants of the Tarantaise. H. W.

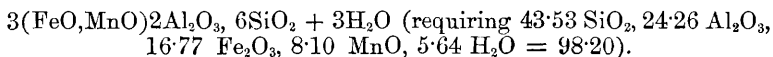
A New Locality of Szaboite. By F. GONNARD (*Jahrb. f. Min.*, 1880, 1, Ref. 346).—The author has found szaboite in the lava of the neighbourhood of Biancavilla, therefore near the locality mentioned by v. Lasaulx, viz., Monte Calvario, and points out that the crystals from the former locality are distinguished by their pearl-grey colour

from the otherwise similar crystals of the chocolate-brown variety from Monte Calvario and the Arany mountain, as well as from the sphene-yellow crystals of the Riveau-Grand, Monte Dore (this Journal, **38**, 225), whilst the mineral from the Arany mountain consists, according to Koch's analysis, of a ferric silicate containing small quantities of alumina and lime, and the crystals from Monte Calvario, to judge from their colour, have a similar composition; the author thinks that the szaboite discovered by himself will probably yield the pure calcio-aluminic compound, and that the specimens from Riveau-Grand are probably of intermediate composition. H. W.

Note on Venasquite. By A. DAMOUR (*Jahrb. f. Min.*, 1880, **1**, Ref. 348).—Nérée, in his work entitled *Bains et Courses de Luchon*, 1857, mentions a mineral from the neighbourhood of Venasque, in the Pyrenees, which he associates with ottrelite. This mineral occurs in laminar and radio-crystalline masses, exhibiting distinct cleavage. It is opaque, and of grey-black colour. $H. = 5.5$; sp. gr. $= 3.26$. Heated in a matrass, it gives off water. Before the blowpipe it melts only on the thin edges; on charcoal it yields a slightly magnetic bead, and with phosphorus salt it gives the iron reaction, and leaves a skeleton of silica. It is not attacked by acids. Its analysis gave—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	H ₂ O.
44.79	29.71	20.75	0.62	4.93 = 100.80

leading to the formula $(FeO, MgO)Al_2O_3, 3SiO_2 + H_2O$. This analysis does not agree with that given by the author, in 1842, for ottrelite, from Luxemburg, for which he deduced the formula—



The chief distinction between the two minerals is the considerable percentage of manganous oxide in attrelite. H. W.

Parallel Combination of Different Varieties of Epidote. By M. O. BAUER (*Jahrb. f. Min.*, 1880, **1**, Mem. 78—82).—It has long been known that the several varieties of epidote, though agreeing perfectly in their general relations, nevertheless exhibit considerable differences of chemical composition and crystalline form, crystals from various localities often differing in the magnitude of their corresponding angles, as well as in their colour. As regards their chemical composition, all epidotes contain alumina and ferric oxide, but in very different proportions, and, according to Ludwig (*Tschermak's Mineral. Mittheil.*, **2**, 187), these chemical differences may be explained by assuming that, as in the plagioclases, a certain number of molecules of terminal number free from alumina, viz., iron-epidote, $Si_6Fe_6Ca_4H_2O_{26}$, is united in isomorphous mixture with a certain quantity of aluminium epidote, $Si_6Al_6Ca_4H_2O_{26}$. In fact all good analyses of epidote, like those of plagioclase, may be calculated on this principle, that an approximate estimate of the composition of an epidote may be deduced even from its colour, inasmuch as the mixtures very rich in iron

epidote have a dark bottle-green colour, whereas those in which the aluminium epidote greatly predominates are light yellow or greenish or reddish-yellow. The same relations serve to explain the crystallo-graphic difference, which, as in other isomorphous mixtures, affect only the magnitudes of the corresponding angles.

The isomorphism of the different varieties of epidote is further shown by the occasional occurrence of parallel combinations of very light and very dark-coloured combinations of epidote crystals. Crystals exhibiting this parallel attachment are found at Zöptau in Moravia, where the dark-green crystals are more or less covered by light-green epidote crystals. In the following Table, No. I gives the composition of the light-green crystals, which shows that they are composed of 80 per cent. aluminium and 20 per cent. iron-epidote; II shows the calculated percentage composition of such a mixture; and III gives the composition of the dark-green crystals, which is that of a mixture of 60 per cent. aluminium and 40 iron-epidote.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	H ₂ O.
I..	39.18	26.52	8.21	23.89	2.20 = 100
II..	38.29	27.10	8.87	23.82	1.92 = 100
III..	38.51	18.88	17.25	23.32	2.98 = 100.94

A comparison of the analyses of these and other epidotes shows that the parallel combination above described is formed of one of the most ferruginous, and one of the least ferruginous, epidotes hitherto known.

H. W.

Pyroxene from Nordmark in Sweden. By H. SJÖGREN (*Jahrb. f. Min.*, 1880, 2, Ref. 15).—The crystals examined were obtained from iron mines, where they occur sometimes isolated, sometimes grouped in beautiful geodes: they are often covered with an argillaceous mud, or imbedded therein. They are usually from 1 to 2 cm. long, too large therefore to be measured with the reflecting goniometer; they are but seldom completely developed at both ends. Nearly half of them exhibit only four forms, $\infty P\infty$, $\infty P\infty$, $P\infty$, $0P$; the first three being greatly predominant. The type is mostly compressed parallelopipedal, sometimes prismatic in the direction of the vertical axis or tabular to predominance of $\infty P\infty$. Cleavage parallel to ∞P and $\infty P\infty$, the former very distinct, the latter scarcely perceptible. Fracture and cleavage-faces dark-green to blackish-green; natural faces, velvet-black; plates in transmitted light, grass to emerald-green.

The Nordmark pyroxene was first analysed in 1846 by Funck, afterwards by H. Rose, and has lately been analysed by Doelter (I) and by Sjögren (II) with the following results:—

	SiO ₂ .	CaO.	MgO.	FeO.	MnO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Sp. gr.
I...	51.05	22.44	5.92	17.31	0.60	0.95	1.10 = 99.37	3.367
II...	50.91	22.93	7.21	17.34	0.21	0.76	0.17 = 99.53	3.311

Hence, according to Tschermak's system—

I.	II.
16CaFeSi ₂ O ₆	38CaFeSi ₂ O ₆
8MgCaSi ₂ O ₆	27MgCaSi ₂ O ₆
1MgR ₂ SiO ₆	1MgR ₂ SiO ₆

Morphologically this pyroxene is most nearly related to diopside, and is intermediate between malacolite and hedenbergite; Des Cloizeaux refers it to the latter, whereas Erdmann designates it as malacolite. H. W.

Idocrase from Gleinitz and the Johnsberg, near Jordansmühl. By A. v. LASAULX (*Jahrb. f. Min.*, 1880, 2, Ref., 143).—Websky some time ago found thick crusts of yellowish and peach-red idocrase in a mica-slate at the south-west foot of the Johnsberg between Trebnig and Wütterisch; he also mentions drusy aggregates of bluish idocrase in small prisms, terminated by ditetragonal pyramids, from the cliffs of Gleinitz and Jordansmühl. According to v. Lasaulx, the prisms projecting from the dense groups exhibit a very distinct polar coloration, as well as pleochroism, weaker or stronger according to the colour (colourless, light-greenish, roseate, amethyst-blue).

The crystals exhibit the following three combinations:—(1.) $\infty P. \infty P. \infty P.$; prisms strongly striated by $\infty P2$. (2.) $\infty P. 3P3$, rarely with P; primary polar edge-angle of $3P3 = 134^\circ 44' 30''$. (3.) $P. P\infty, 0P$ (rarely, but then with all the faces developed).

Analyses of transparent and colourless material from Gleintz (I), and of roseate crystals from the Johnsberg (II), and an earlier analysis (III), by Websky, of material from the latter locality, gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	MnO.	Na ₂ O.	H ₂ O.
37·57	16·30	1·82	2·76	36·26	1·75	—	undet.	3·01 = 99·47
37·32	16·87	2·57	2·38	34·46	0·67	3·23	—	2·22 = 99·72
39·41*	19·63	—	2·42	34·75	0·38	3·41	—	— = 100·00

* Loss.

The roseate colour of the Johnsberg crystals may, therefore, be attributed to the manganous oxide which replaces part of the lime and other monoxides, and accordingly this variety may be designated as manganidocrase. H. W.

Mineralogical Notices. By C. U. SHEPARD (*Sill. Jour.* [3], 20, 54).—*A Peculiar Mineral of the Scapolite Family.*—This mineral occurs crystallised in the bluish-grey saccharine limestone of Galway, Ontario, Canada. The crystals are long prisms, generally square, the larger specimens octangular, the terminations generally undefined; thickness varies from one inch to one-eighth inch, and is generally regular throughout (one specimen was acuminate). The surfaces of the crystals are fairly smooth, without striation; colour black, with slight intermixture of grey and blue; where the blue colour occurs, the crystals are semi-transparent, but generally they are only translucent on the edges. Vertical cleavage distinct, parallel with the narrower planes of the primary prisms. The larger crystals are interlaminated with calcite. Hardness 7·0 to 7·5. Sp. gr. 2·608. When powdered, the crystals

emit a foetid odour, due to organic matter, which, together with free carbon, may be burnt off by ignition for several hours.

The analysis of the mineral gives very discordant results—

SiO ₂ .	Al ₂ O ₃ .	CaO.	SiO ₂ .
48·65—51·3	13·45—19·62	17·43—21·6	4·35—5·21
Na ₂ O.	K ₂ O.	MgO.	
4·35	1·109	0·468	

The alkalis and the magnesia were obtained in a single analysis.

This mineral differs essentially from scapolite, and is perhaps the original mineral from which couseranite and dipyre have been derived by hydration. The author proposes to name it *Ontariolite*, supposing it to be a new species.

Cassiterite has been found at Coosa, Alabama, in well-formed octohedral crystals, showing, however, narrow faces of the ordinary prism.

Yttrotantalite.—One crystal found with the above. Its form is that of a right rhombic prism of about 122°, having its acute terminal angles replaced by two planes, inclining to one another across the obtuse lateral edge of the prism, at an angle of nearly 125°. Sp. gr. = 6·001.

Paracolumbite.—The author proposes to change the name of this mineral to *para-ilmenite*, as its composition approaches that of ilmenite, whilst it differs in its sp. gr. and fusibility.

Hemihedral forms of Staurolite.—Among the crystals from Morganton, Georgia, hemihedral forms are not unfrequent. The hemihedrism relates to the alternate obtuse terminal angles which are replaced by broad single planes.

Fergusonite, Rutherfordite.—A few small crystals of this mineral have been found among the samarskite from Mitchell Co., North Carolina. The author now considers that the mineral named by him *Rutherfordite* is referable to *fergusonite*.

Green Pagodite from Georgia.—A handsome building stone of an apple-green to emerald-green colour, sometimes mixed with red rutile and interlaminated with muscovite. Hardness = 3. Sp. gr. = 2·86. Composition—

SiO ₂ .	Al ₂ O ₃ .	FeO.	Na ₂ O.	K ₂ O.	H ₂ O.
48—52	22·6—34	2·10	5·12	4·43	3·5

Chromium and titanio acid not determined.

C. W. W.

Mineralogy of the Counties of Dublin and Wicklow.

By S. HAUGHTON (*Journal of the Royal Geological Society of Ireland*, 1878, 5, New Series; *Jahrb. f. Min.*, 1880, 1, Ref. 155—157).—

(1.) *Minerals from the Granites of Dublin and Wicklow*.—The constituent minerals are quartz, orthoclase, albite, potash-mica (margarodite), and lepidomelane. The potash-mica occurs in prisms and tables of rhombic or hexagonal aspect. It is biaxial: plane of optic axes parallel to the longer diagonal of the rhombs of 120°; the apparent angle of the axes in air varies in the different varieties from 53° 8' to 76° 15'. Chemically, this mineral differs from muscovite chiefly in

the amount of water. The lepidomelane occurs in six-sided tables, and is described as uniaxial, a statement, which, according to more recent investigations, must be interpreted as biaxial with a very small axial angle. It dissolves completely in hydrochloric acid. At Ballyellin (Carlow County), regular intergrowths with margarodite occur.

The composition of these feldspars and micas is as follows:—

	Orthoclase.	Albite.	Margarodite.	Lepidomelane.
SiO ₂	64.59	64.70	44.58	35.55
Al ₂ O ₃	18.31	21.80	32.13	17.08
Fe ₂ O ₃	—	—	4.57	23.70
CaO	0.25	—	0.78	0.61
MgO.....	0.58	—	0.76	3.07
K ₂ O	12.23	2.84	10.67	9.45
Na ₂ O.....	2.75	9.78	0.95	0.35
FeO	—	—	—	3.55
MnO.....	—	CaF ₂ 0.80	—	1.95
Loss by ignition ..	0.58	—	5.34	4.30
	99.29	99.92	99.78	99.61

The granite extends from Rockabill, near Poulmounty, *i.e.*, from N.N.E. to S.S.W. Hand specimens of the rock taken at suitable intervals, gave the following mean composition:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss by ignition.
72.07	14.81	2.25	1.63	0.33	5.11	2.79	1.09 = 100.08

From this composition and that of the constituent minerals, Haughton deduces for the mean proximate constitution of the granite: 32.57 per cent. quartz, 15.44 orthoclase, 22.10 albite, 19.16 margarodite, 5.81 lepidomelane, 4.92 calcium silicate. Occasional constituents of this granite are: beryl, spodumene fresh and decomposed, tourmaline, garnet, fluor spar, apatite, agalmatolite.

(2.) *Minerals of the Metamorphic Slates of Dublin and Wicklow.*—Besides mica and hornblende, which are the chief constituents of these slates, the following minerals have been observed: Andalusite, chialstolite, staurolite, hornblende, jasper, Mocha-stone, zircon, gold, magnetite, chlorite, spinell, platinum, wood-tin. Remarkable is the absence of garnet, idocrase, and other calcium silicates.

(3.) *Minerals of the Carboniferous Limestone of Dublin County.*—Lydian stone, iron pyrites, asphalt, anthraconite.

(4.) *Minerals occurring in the Mines of the Counties Wicklow and Dublin.*—Iron pyrites, fluor spar, *schieferspath*, heavy spar, silver, horn-silver, brown iron ore, manganese oxides, copper, copper pyrites, tinstone, carbonate sulphate and phosphate of lead, galena, and blende.

H. W.

Artificial Production of a Felspathic Substance. By C. FRIEDEL and E. SARASIN (*Jahrb. f. Min.*, 1880, 2, Ref. 154).—In the preparation of crystalline quartz (p. 346), the authors constantly obtained small rhombic tablets, which they have since produced, accompanied by only a small quantity of quartz, by increasing the

proportions of alumina and potash used in the preparation, or, more readily, by precipitating aluminium chloride with a silicate of potassium containing a large proportion of silica, washing the precipitate thoroughly, and adding a small quantity of potash together with potassium silicate. This mixture heated for 36 hours to a temperature short of dull redness, then exhausted with *aqua regia*, and freed from the lighter particles by levigation, yielded rectangular or irregular six-sided tablets.

Before the blowpipe, this product melts like felspar to a white blistered glass. Its density is exactly that of orthoclase. Its analysis gave the composition of a felspathic substance, which may be regarded either as ordinary felspar mixed with quartz, or as a highly silicious felspar analogous to petalite, mixed with a small quantity of quartz.

		Calculated for	
		Orthoclase.	Potassic petalite.
SiO ₂	72.0	64.63	70.90
Al ₂ O ₃	14.9	18.49	15.21
K ₂ O.....	12.2	16.87	13.88
		<hr/> 99.1	

Microscopical examination showed enclosed quartz, but the quantity of it was too small to be decisive in favour of the first view. In polarised light, the tablets exhibited a monoclinic character, but the double refraction was not strong enough to give distinct indications as to the nature of the felspar.

In two experiments made at a higher temperature, the authors obtained, together with crystallised quartz, hexagonal tablets, having the characteristic properties of tridymite. H. W.

Corundiferous Felspar of Biella, in Piedmont. By A. COSSA (*Jahrb. f. Min.*, 1880, 1, Ref. 173).—This felspar, which forms veins in the diorite of the district, is white, compact, and laminar. Sp. gr. 2.628 at 17°. Melts with tolerable facility to a colourless glass. Not decomposed by hydrochloric acid. Loss by ignition (H₂O) = 0.294. An analysis by Rocholl (*Rammelsberg's Mineralchemie*, 2te Aufl., p. 575) of material from Petinengo, near Turin, gave—

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.
62.52	22.40	2.29	10.78	1.19 = 99.18

Cossa's analysis differs but little from this, but he found in addition traces of TiO₂, Fe₂O₃, and P₂O₅, and spectral analysis showed the presence of Li, Cs, and Rb.

Under the microscope, this felspar presents the appearance of a microcrystalline mixture, with irregularly formed and irregularly imbedded fragments of plagioclase, which are much decomposed, and only partially exhibit the characteristic twin-striation. Many crystals exhibit a fine grating-pattern, like the so-called microline. Small crystals of apatite, and irregularly imbedded fluid cavities, some with movable bubbles, are of frequent occurrence. These bubbles do not disappear on heating. Amorphous granular matter insoluble in hydro-

chloric acid renders the felspar opaque in many parts; spots of ferrite are also present, together with black amorphous bodies of unknown composition.

The corundum (sp. gr. = 3·842 at 17°) imbedded in this felspar is much harder than emery; it gives off but little water on ignition, but is readily turned yellowish thereby. Unlike the corundum of India, it does not contain a trace of magnetite. Its analysis gave—

Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ *.	CaO.	H ₂ O.
99·725	1·094	3·141	trace	0·867 = 98·627

* With distinct trace of TiO₂.

H. W.

Haughtonite, a New Mica. By M. FORSTER HEDDLE (*Mineralogical Magazine*, 1879, No. 13, 72; *Jahrb. f. Min.*, 1880, I, Ref. 341).—This mineral occurs in the granite of many parts of Scotland. It is very closely related to biotite and lepidomelane, differing from the first, however, by its small amount of magnesia, and from the second by its large proportion of ferrous oxide. The three minerals also resemble each other very closely in their physical properties, haughtonite being somewhat harder and heavier than lepidomelane, which therefore occupies a position intermediate between haughtonite and biotite.

Haughtonite occurs in crystals of all sizes up to a foot long, forming either more or less distinct six-sided tables with orthorhombic habit, or, more frequently, distorted individuals or groups of intergrown laminae. Colour pitch- or brown-black to clove-brown, greenish tints occurring but rarely. The cleavage-lamellae often exhibit a brown or reddish translucence. It has a strong vitreous lustre in the fresh state, fatty when weathered. The crystals are for the most part slightly biaxial.

The mineral is always found in beds or veins of granite and felspar occurring in gneisses, especially those which are much metamorphosed, also in the granite and diorite of the north of Scotland. It is especially characteristic of the grey granite of Aberdeenshire, the beds and veins of which always contain it in large plates; muscovite does not occur at all in this granite. Haughtonite is almost always accompanied by oligoclase, and frequently by sphene and allanite.

The following table exhibits the composition of haughtonite as the mean of numerous analyses; also the oxygen-ratios calculated therefrom, as compared with those of biotite and lepidomelane:—

Haughtonite.		Oxygen.			Biotite.	Lepidome- lane.
SiO ₂	35·93	19·16	19·16	19	21	20
Al ₂ O ₃	18·06	8·41	} 0·78	10	8	15·5
Fe ₂ O ₃	4·55	1·37				
FeO	17·22	3·80	} 12·67	12·5	15	7
MnO	0·81	0·18				
CaO	1·48	0·42				
MgO	9·07	3·63				
K ₂ O	8·49	1·44	} 0·29			
Na ₂ O	1·13	0·29				
H ₂ O	3·27	2·91				

From five older analyses, the mean of which agrees very nearly with the above, it appears that haughtonite has been previously examined, though not hitherto recognised as a distinct mineral species.

Before the blowpipe, it melts with difficulty to a strongly magnetic bead, the laminae after heating becoming deep black, whereas biotite and lepidomelane become paler in colour. By acids, haughtonite is less quickly decomposed than the other two minerals, incompletely by hydrochloric acid, completely by sulphuric acid, with separation of silica in shining scales. In consequence of the large proportion of ferrous oxide which it contains, it is more susceptible of atmospheric influences than other micas. H. W.

Oligoclase from Dürrmosbach. By K. HAUSHOFER (*Jahrb. f. Min.*, 1880, 1, Ref. 349).—The mineral from Dürrmosbach, near Aschaffenburg, hitherto known as labradorite, appears, when examined in thin section, to be composed of two substances, one clear, the other turbid. In polarised light the former, which constitutes the greater part of the mineral, is seen to consist of separate crystals in various orientation, while the latter has the appearance of groups. In the clearer portions, a striation characteristic of plagioclase may sometimes be seen, even without the aid of the microscope. The mineral, which is white, rose-coloured, or violet, exhibits in the coloured varieties enclosures of black manganese oxides (manganite?). Sp. gr. 2·663. Cleavage not determinable with exactness. Loss by ignition 1·29 and 1·52 per cent. for the white variety, 1·80 per cent. for the reddish masses. Two analyses of the white substance gave: *a*, by decomposition with alkaline carbonate; *b*, with hydrofluoric acid:—

SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.
59·30	25·75	4·79	2·78*	5·63*	1·29 = 99·54
59·17*	26·20*	4·70	2·78	5·63	1·52 = 100·00

* Determined by loss.

These numbers show that the felspar is nearer to oligoclase than to labradorite—

Na : Ca = 2 : 1 (or exactly 1·81 : 0·85) and Al₂ : Si = 1 : 3·9

The calculation of this felspar according to Tschermak's theory presents difficulties, the silica and alumina being found to be in excess of the bases. Moreover, the water must be reckoned as an essential constituent, inasmuch as no "pore-enclosures," &c., were found in the mineral. The calculation was therefore made in two ways, the hydrogen being first included in the formula of a silicate constituted like anorthite, and the water being further regarded as a constituent of a silicate resembling kaolin, Si₂Al₂H₄O₉.

On these bases, the composition of the oligoclase of Dürrmosbach may be calculated as follows:—

	SiO ₂ .	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	CaO.	H ₂ O.
16·4 p. c. potash-felspar =	10·6	3·0	2·78	—	—	—
47·6 „ soda-felspar =	32·6	9·3	—	5·63	—	—
23·8 „ lime-felspar =	10·2	8·7	—	—	4·79	—
12·2 „ Si ₄ Al ₄ H ₄ O ₁₆ =	6·2	5·2	—	—	—	0·9
	59·6	26·2	2·78	5·63	4·79	0·9

or, instead of the last component—

12·2 p. c. Si ₂ Al ₂ H ₄ O ₉ =	5·7	4·8	—	—	—	1·5
	59·1	25·8	2·78	5·63	4·79	1·5

values which approach very nearly to the results of analysis.

The white mineral, when exposed in the state of powder to air and sunlight, acquires, like window-glass rich in manganous oxide, a rose-red colour.

H. W.

The Picrites of Nassau and the Labradorite Porphyries of Westphalia. By G. ANGELBIS (*Jahrb. f. Min.*, 1880, 2, Ref. 73).—The picrites (diorites of Koch, greenstones of v. Dechen, hypersthene of v. Dechen, in part) are found on numerous elevations on the north side of the band of diabase which stretches from S.W. to N.E. in the hypodevonian formation of Nassau. The chemical composition has been determined by analysis of the rocks of Burg (I and II) and of Nieder-Dieten (III).

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.
I	40·37	9·86	4·76	8·34	4·74	21·63
II	40·37	10·02	—	13·74	4·58	21·93
III	39·56	8·47	5·36	10·32	4·91	24·82
			K ₂ O.	Na ₂ O.	H ₂ O.	
I			0·82	3·61	5·04	= 99·17
II			0·82	3·61	5·04	= 100·11
III	not determined				5·05	

The Nieder-Dieten rock gave also traces of phosphoric and titanitic acids. The amount of alkalis, which is not inconsiderable, points distinctly to the presence of small quantities of plagioclase, which were also detected by the microscope.

The labradorite-porphyries from the Devonian strata of Westphalia appear, from the microscopic examinations of Angelbis, to be porphyritic normal diabases with a large proportion of calcite. The author has analysed the plagioclases from a rock of this character occurring to the south of Brilon, with the following result:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Loss by ignition.
51·27	28·74—28·51	0·91—0·83	9·86—10·05	2·32	3·85	1·83

This plagioclase is therefore a labradorite very rich in potash, whereas the plagioclase which penetrated the rock of Gevelinghausen, and was analysed by Rammelsberg, is an oligoclase. H. W.

Note on an Olivine-gabbro from Cornwall. By T. S. HAUGHTON (*Geol. Mag.*, 6, 504; *Jahrb. f. Min.*, 1880, 2, Ref. 72).—An olivine-gabbro from Coversack, in Cornwall, described by Bonney (*Geol. Soc. Qu. J.*, 1877, 906), and closely resembling the "Forellenstein" of Volpersdorf, was found by the author of this paper to be nearly free from pyroxene. Analysis I gives the composition of the rock as determined by decomposition with alkalis: II that of the portion soluble in hydrochloric acid: III, that of the purest plagioclase that could be separated from the rock. This, like the feldspar of the Volpersdorf rock, appears to belong to the Bytownite series.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.
I	45·73	22·10	0·71	3·51	9·26	11·46
II	44·81	21·62	0·86	3·73	9·19	11·78
III	46·95	29·35	0·59		12·18	0·46

	K ₂ O.	Na ₂ O.	H ₂ O.	Residue.	
I	0·34	2·54	4·38	—	= 100·03
II	0·35	2·30	3·96	3·17	= 101·77
III	0·48	3·61	3·19	—	= 99·51

H. W.

Peridotiferous Diabase of Mosso, in the Biellese. By A. COSSA (*Jahrb. f. Min.*, 1880, 2, Ref. 71).—At Mosso, in the neighbourhood of Biella, in Piedmont, there occurs in blocks lying on the surface or buried a little below it, a fine-grained diabase, together with small quantities of biotite and amphibole. The augite, as frequently observed in allied rocks, is distinguished by bright pleochroism. Sp. gr. at 9° between 2·932 and 2·973. Analysis gave—

SiO ₂ .*	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.†.	CaO.	MgO.
48·18	0·37	18·86	6·22	2·27	9·95	8·46

Na ₂ O.	K ₂ O.	X.‡
3·88	1·23	0·45 = 99·87

H. W.

Hypersthene from the Pumice of Santorin. By F. FOUQUÉ (*Jahrb. f. Min.*, 1880, 2, Ref. 75).—By treating this pumice with hydrochloric acid, the vitreous mass is rapidly and completely decomposed; but if the process is interrupted at the proper time, the crystals which have separated from it remain intact. The crystals consist of small prisms of hypersthene (up to 0·7 mm. long and 0·1 mm. thick), in which the faces ∞P , $\infty P\infty$, $\infty P\infty$, $\infty P\bar{3}$, $\infty P\bar{2}$, and $\infty P\bar{2}$ of the prismatic zone could be measured, whereas the terminal faces were too small for measurement; in all the faces of the prismatic zone,

* With trace of TiO₂.

† With traces of MnO, NiO and CoO.

‡ Loss by ignition.

pleochroism and extinction in the direction of the principal axis could be detected. The analysis of a hypersthene of sp. gr. 3·485 gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	
49·8	2·3	0·8	25·0	10·8	11·2	0·5	= 100·4

The hypersthene was accompanied by a green transparent true monoclinic augite, to which the lime and alumina in the above analysis may perhaps be due. Amongst the separated crystals there were also two triclinic feldspars (one of which was oligoclase) and magnetite. The pumice-glass has the following composition :—

SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.
71·0	0·5	0·8	16·8	0·8	0·7	7·4	2·0 = 100

It is not stated whether the glass was actually free from water, which would be very remarkable, or whether the composition was calculated on the substance regarded as anhydrous. H. W.

A Potassio-ferric Silicate analogous to Leucite. By P. HAUTEFEUILLE (*Compt. rend.*, 90, 378).—This compound is prepared, like the silicates of aluminium and lithium already described (this Journal, 1880, 38, 487), by heating a mixture of silica and ferric oxide with potassium vanadate to the melting point of silver. Small greenish-yellow transparent crystals are thereby formed, which gradually become larger, and may be obtained free from all admixtures by adding to the mass, after the amorphous constituents have been dissolved out, about one-hundredth of its weight of potassium silicofluoride. The small crystals are completely decomposed by sulphuric acid, and give by analysis 49·66 per cent. SiO₂, 32·13 Fe₂O₃, and 17·53 K₂O, agreeing nearly with the formula K₂O, Fe₂O₃, 4SiO₂, which is analogous to that of leucite, K₂O, Al₂O₃, 4SiO₂.

The crystals are apparently icositetrahedrons, but they are actually not regular, but quadratic, like leucite (this Journal, 1873, 1007), exhibiting the combination P. 4P2. They are strongly double refracting, and exhibit twin lamellæ and the consequent optical peculiarities, like natural leucite.

The formation of these crystals requires a somewhat higher temperature than that of ordinary feldspar. When a mixture of alumina, ferric oxide, silica, and potassium vanadate is heated, it may happen that only feldspar is produced and no leucite, if the temperature is so regulated, that the potassium vanadate does not attack the ferric oxide. H. W.

Penwithite, a new Cornish Mineral. By J. H. COLLINS (*Mineralogical Magazine*, 1878, No. 9, 91, and No. 13, 89; *Jahrb. f. Min.*, 1880, 1, Ref. 341).—This mineral occurs with quartz and brown spar (manganous carbonate), in the mining district of Penwith, West Cornwall. It is transparent, with strong vitreous lustre and dark amber to reddish-brown colour. H. = 3·5. Sp. gr. = 2·49. Brittle with distinct conchoidal fracture. Heated in a test-tube it gives off

water, but otherwise remains unaltered. Before the blowpipe, it melts on the edges. Hydrochloric acid dissolves out the whole of the manganese, leaving nearly colourless silica.

Chemical composition—

H ₂ O.	SiO ₂ .	MnO.	FeO.	U ₂ O ₃ .	Cu.
21·80	36·40	37·62	2·52	0·30	trace = 98·64

Hence, regarding the iron and uranium as replacing part of the manganese, the mineral may be represented by the formula—

MnSiO₃ + 2H₂O, which requires MnO 42·5, SiO₂ 35·9, and 21·5 H₂O.
H. W.

A Contribution to South American Geology. By G. ATTWOOD, with an Appendix by T. G. BONNEY (*Geol. Soc. Qu. J.*, **35**, 582—590; *Jahrb. f. Min.*, 1880, **2**, Ref. 57).—This paper contains a description of the rocks occurring between Puerto de Tablas on the Orinoco and the gold district of Caratal. These rocks consist of gneisses and azoic slates, together with huge granite masses and a few basic eruptive rocks. Quartz-veins are of frequent occurrence in all of them, but they are auriferous only where they are situated in a rock called *diabase*, which is very widely diffused in the district of Caratal. This rock is fine-grained, destitute of pebbles, of greenish colour, and consists of felspar (plagioclase), augite, chlorite, and ilmenite or magnetite, or the products of decomposition of these minerals, together with traces of the sulphides of iron and copper. In the following analyses, I relates to the fresh rock, II to a weathered, and III to a much-weathered variety. The samples were obtained from the mines of the Potosi Company.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.
I..	49·57	15·37	—	12·34	9·65	7·41	0·85
II..	41·77	19·34	13·21	4·63	4·98	5·01	0·69
III..	43·46	18·39	20·43	—	2·37	3·46	0·59

	Na ₂ O.	H ₂ O.*	H ₂ O.†
I...	1·99	3·10	0·17 = 100·45
II...	0·83	7·30	2·55 = 100·31
III...	0·14	7·95	3·39 = 100·18

Also traces of manganese, copper, sulphur, and chlorine. The analyses show with great clearness the normal progress of the decomposition of basic eruptive rocks.
H. W.

Fossil Plants from the Carboniferous Strata of the Tarentaise. By C. W. GÜMBEL (*Jahrb. f. Min.*, 1880, **2**, Ref. 78).—The plants of this formation have been petrified by a mineral substance closely resembling the material of the graptolite petrifications. It forms thin scaly laminæ, sometimes elastically flexible, white with nacreous lustre, and feeling like talc. H. = 1. Sp. gr. 2·8. Before the blowpipe, it fuses to a mass which exfoliates like a cauliflower-

* Combined.

† Hygroscopic.

head, turns blue with cobalt solution, and is not completely decomposed by sulphuric acid. Its analysis (I) shows an unmistakeable resemblance to that of the slate (II) in which the plants are imbedded; whilst III is a new analysis (given for comparison) by Gumbel of the graptolite substance, from Gräfenenthal, in the Thüringerwald.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.
I..	49·71	1·035	28·62	2·688	trace	trace	1·60
II..	56·80	0·70	25·45	3·05	—	trace	1·63
III..	52·50	1·00	29·50	3·50	—	trace	1·16

	K ₂ O.	Na ₂ O.	Water and charcoal.	
I....	6·803	2·208	7·384	= 100·048
II....	4·20	1·36	8·00	= 100·59
III....	5·06		7·75	= 7·75

H. W.

Rocks of Kerguelen's Land and the Neighbouring Islands. By C. W. GÜMBEL (*Jahrb. f. Min.*, 1880, 2, Ref. 77).—I. A much decomposed basaltic lava from Kerguelen's Land, the cavities of which contained fine analcimes, together with carbonates and silicious minerals, gave by analysis—

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	H ₂ O.
56·06	22·68	0·38	0·14	12·94	8·48 = 100·68

II. From Christmas Harbour in the same island, there was obtained an apparently palagonitic substance of sp. gr. 2·78; hardness 4·5, with black-brown colour and pitchy lustre, which occurs there together with lignite. On the ground of its optical character (isotropic), and of an incomplete analysis, Gumbel regards this substance as allied to hisingerite or thaulite.

III. A phenolite from Fernando de Noronha, yielding 32·2 per cent. soluble in hydrochloric acid (A), and 67·8 per cent. insoluble residue (B), gave by analysis:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.
A ..	47·54	30·93	3·57	0·24	1·59	13·74	2·00	1·18 = 100·79
B ..	65·08	19·24	3·52	0·62	0·73	3·99	6·27	0·52 = 99·97

H. W.

Phosphoritic Limestones of the Island of Bonaire, West Indies. By K. MARTIN (*Jahrb. f. Min.*, 1880, 1, Ref. 335).—These limestones are mostly yellowish-brown, also red- and brown-grey, less frequently white and porous, often spongy, sometimes with larger separate cavities lined with botryoidal phosphorite and sometimes completely filled with it, the filling material being distinguished from the principal mass by its colour.

The rock contains between 50 and 76 per cent. calcium phosphate, together with calcium carbonate, always in inverse ratio to the phosphate, the variously constituted varieties in all the localities being irregularly mixed. The phosphorites occur in veins and detached masses from 3 to 16 cm. thick, in a limestone containing from 6 to 7

per cent. calcium phosphate, which sometimes contains corals, and is thence called by the author "coral-limestone," the entire group of these limestones containing phosphoric acid being called "phosphoritic limestones" (analogous to dolomitic limestones).

The phosphorites sometimes contain remains of molluscs, and in larger quantity sharks' teeth and remains of bones, sometimes also traces of corals. The fishes, one species of which is still existing, while another is of the tertiary period, indicate that the rocks are of comparatively recent date. Their origin is attributed by the author to the breaking-up of coral-reefs which formerly surrounded the island, and to which, as to Sombbrero, phosphoric acid was conveyed from beds of guano, which in fact occur on the island, though at some distance from the phosphorites, the residues of the guano-mass having been afterwards washed away. Similar phosphorites occur also on the islands Arabu and Curaçao, and are used for technical purposes.

H. W.

Lavas from Hawaii and other Islands of the Pacific Ocean.

By E. COHEN (*Jahrb. f. Min.*, 1880, 2, Mem. 23—62).—1. *Compact Basalt Obsidian*.—Black, pitchy-lustrous, microscopically homogeneous lava, having a decidedly conchoidal fracture, and compact, with the exception of a few small pores appearing like needle-points. Microscopic examinations show a rather light yellow glass with numerous anisotropic microliths. There are also a few interspersed crystals of olivine, augite, and plagioclase.

2. *Tumefied Obsidian, Kilauea Lava of 1843*.—A black, pitchy-lustrous glass, very rich in round cavities, and covered on the surface with a network of thin iridescent glass-fibres. Under the microscope, this variety appears very much like the preceding, interspersed crystals, consisting of olivine and plagioclase, being, however, somewhat more numerous.

3. *Lavas from Mauna Loa, 1854*.—These lavas form finely porous plates $\frac{1}{2}$ to 1 cm. thick, smooth and shining on one side, while the other side is scoriaceous and covered with fine glass threads. Under the microscope, the light brownish glass appears very rich in forked microlites with capillary appendages, and in thin rhombic plates.

4. *Large-pored Pumice-like Basalt-obsidian*.—Appears under the microscope very rich in dark-brown concretions. Microlites and rhombic plates are wanting, but are replaced by globulites 0.002 mm. in diameter. There are also a few interspersed crystals of olivine, augite, and plagioclase.

5. *Basaltic Pumice*.—Very frothy lava of light greyish-brown colour, scoriaceous on the surface, and covered with a thin fused crust like a brown glaze.

6. *Capillary Basalt-pumice*; so-called *Pélé's Hair*.—The fine threads, some having a diameter of only $\frac{1}{160}$ mm., occasionally attain the length of a meter. The surface is mostly quite smooth, sometimes however finely striated. Only a few of the threads are compact throughout, and free from products of devitrification.

7. *Scoriaceous Porous Basalt-obsidian from Niuaufou*.—Consists in parts of glass as pure as that of the pumice from Mauna Loa; more frequently, however, the thin partitions of the macroscopic cavities

inclose numerous round or oval closed gas-pores, and isolated double-refracting microlites with rectangular outline.

8. *Augite-andesite Pumice*.—Raised from the sea-bottom between New Britain and New Ireland. It is frothy, of light yellowish-grey colour, deceptively like many Liparian pumices. The cavities are sometimes much elongated, so that many parts have a fibrous aspect. The glass incloses grains of augite and plagioclase, or aggregates of these two minerals with magnetite. Under the microscope it appears very rich in ellipsoidal, pen-shaped, or variously distorted vapour-pores, and minute cauliform double-refracting microlites.

The analyses of these lavas gave the following results:—

	1	2	3	4	5	6	7	8
Silica	53·81	51·41	51·17	{ 52·39 2·73	51·12	50·82	50·74	62·29
Titanic oxide	2·01	2·61			—*	—*	1·68	0·80
Alumina	13·48	12·92	28·33	{ 11·55 12·11	10·09	9·14	11·98	15·97
Ferric oxide	3·02	2·87			{ 5·35 8·59	7·33	3·41	3·77
Ferrous oxide....	7·39	9·29	—	—	7·03	7·03	8·11	13·73
Manganous oxide.	trace	0·16			—	0·38	0·54	—
Lime	10·34	11·46	10·43	10·92	9·72	11·63	12·42	4·98
Magnesia	6·46	5·45	9·63	7·10	9·68	7·22	7·25	2·05
Potash	0·64	0·70	—	0·46	0·56	1·02	0·24	2·40
Soda	3·23	2·92	—	2·79	3·38	3·06	2·74	4·80
Water	0·57	0·32	—	—	1·31	1·74	0·52	0·73
	100·95	100·11	—	100·05	99·80	99·37	99·63	101·52
Sp. gr.....	2·75	2·69	—	2·715	2·73	2·66	2·98	—
at	17°	17°	—	16°	16°	19°	—	—

H. W.

Pumice from Launsbach. By V. KOENER (*Jahrb. f. Min.*, 1880, 2, Ref. 74).—During the construction of the railway between Lollar and Wetzlar, there was laid open, to the south of Launsbach and E.S.E. of the Woltersberg, a bed of pumice half a meter thick, imbedded in the clay, and dipping rather steeply towards the south-east. The pumice-sand is brownish-grey, free from clay, and consists of oval and angular grains 0·5 to 1 mm. thick. Analysis by Wachendorff gave the following results:—I. Decomposed by hydrochloric acid. II. By sulphuric acid. III. By sodium carbonate. IV. Mean of all the analyses, exclusive of the residues:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Residue.
I.	43·5	19·1	3·2	1·5	0·4	3·8	3·2	9·4	16·5 = 100·6
II.	2·7	1·9	—	—	—	1·4	—	—	10·4 = 16·4
III.	8·3	1·5	—	—	—	0·6	—	—	— = 10·4
IV.	54·5	22·5	3·2	1·5	0·4	4·9	—	4·1	9·4 = 100·5

H. W.

* In these two analyses, made several years ago, the presence of titanium was overlooked. In Pélé's Hair (No. 6) the author subsequently found titanitic acid quantitatively, its amount being apparently nearly the same as in the other glasses.

Examination of the Material of some French "Vitrified Forts." By DAUBRÉE (*Compt. rend.*, 92, 269—274).—"Vitrified forts" are enceintes or wall-débris, the material of which, consisting—according to the locality—of granite, gneiss, quartzite, clay-slate, basalt, &c., has been cemented together by the aid of fire. They are found in different countries, and usually rest on older rocks, crystalline or non-crystalline, which contain but little lime. A specimen from La Courbe, Orne, consisted of a semi-fused, deep brown slag-like glass, which had no action on polarised light, and contained a large number of transparent octahedrons, probably spinelle, besides other crystals having the physical characteristics of humboldtilite. Analysis indicates that this glass was obtained by adding common salt to an aluminium silicate, such as clay or schist. The analysis of a vitreous, vesicular, fragile, greenish-grey specimen from Sainte Suzanne showed that in this case fusion was effected by the addition of soda to some argillaceous substance. The forts at Puy de Gaudy have been constructed of granite, containing white orthoclase, oligoclase, quartz, and black mica. The specimens have been completely fused on the outside, but the interior still retains the appearance of granite, although the mica has been replaced by a brown opaque vesicular substance, and the felspar has in some cases undergone disintegration. A portion of the felspar has undergone complete fusion, and some of the granite has been changed into innumerable crystals of spinelle and into microlites, which partly consist of triclinic felspar. These alterations have in some cases extended a great distance into the masses of rock employed in the construction of the forts. The mica contains small quantities of fluorine, which would assist in the alteration of the granite, but there is no proof of the addition of any flux, the mean composition of the altered rock being that of an average granite. The examination of these and other specimens shows that fusion was not always effected in the same way, but that the method employed varied according to the materials operated upon. It also shows that the constructors of the forts were experienced in the management of fire, and were acquainted with the means of obtaining and maintaining an intense heat. C. H. B.

Meteorite from Cleborne Co., Alabama, U.S. By W. E. HIDDEN (*Sill. Jour.* [3], 19, 370).—This meteorite was found in 1873. It weighed about 35 lbs., is somewhat triangular in shape, about 25 cm. wide, and 6 cm. thick. Analysis shows it to be the common iron-nickel variety, containing small quantities of copper, phosphorus, and carbon. C. W. W.

Meteoric Iron from Ivanpah, California. By C. U. SHEPARD (*Sill. Jour.* [3], 19, 381).—This meteorite is oval in shape; its entire surface is covered with indentations varying from one to four inches deep; its weight is about 120 lbs. The structure of the mass is highly crystalline; the Widmannstätt figures are plainly visible without etching. The schreibersite present is in very thin leaves and irregular prisms; the latter may be Reichenbach's rhabdite. The composition is Fe = 94.98; Ni = 4.52; P = 0.07; C (as graphite) = 0.10. There is no sulphur present. C. W. W.

The Meteorite of Estherville, Emmet Co., Iowa. By C. U. SHEPARD (*Sill. Jour.* [3], 18, 186).—This meteorite, which fell on the 10th of May, 1879, at 5 P.M., is the third of its kind that has fallen in the State of Iowa since 1847. Its fall, which was observed by several persons, was attended with a terrific explosion, and it penetrated deep into the ground. The principal mass, weighing 431 lbs., was dug up from a depth of 14 feet, and with it were found lumps weighing 32 and 4 lbs., together with smaller pieces. Two miles from this spot a mass, weighing 151 lbs., was dug up from a depth of $4\frac{1}{2}$ feet. The fragments have a burnt edge, and differ greatly in appearance from those of ordinary meteorites.

Nearly two-thirds of the mass consists of chrysolite, in some parts finely crystalline, and of greenish colour; in others more compact, difficult of cleavage, and of a greyer aspect. The stone exhibits no sign of decomposition. Another essential constituent is iron, having a ramified appearance, and sometimes surrounding chrysolite. Schreibersite and Widmanstätt's figures were also recognisable. The iron at the edge of a fragment has sometimes a silver-white colour. The other constituents are troilite and a felspathic mineral, probably an orthite; the variety of olivine called *chassignite* was once recognised; also chromite. The specific gravities of the several parts are as follows:—

Non-metallic portion.	Metallic portion.	Entire meteorite.	Chrysolite.
3.35	5.97	4.54	3.50

These characters show that the meteorite in question is of peculiar character, different from any hitherto known. H. W.

The Emmet County Meteorite. By J. L. SMITH (*Sill. Jour.* [3], 19, 459).—This meteorite was observed to burst when at a considerable height in the air, and a number of fragments, the largest weighing 437 pounds, were collected from an area of about four square miles.

The exterior of the masses is rough, covered with rounded protuberances, which have sometimes a bright metallic lustre, and sometimes consist of lumps of an olive-green mineral. When broken, the meteorite is seen to consist mainly of a grey mineral, bronzite, with the green mineral, olivine, and nodules of metallic iron disseminated through it. The nodules of iron seem to have shrunk away from the enclosing matrix; their composition is:—

Fe.	Ni.	Co.	Cu.	P.
92.001	7.1	0.69	trace	0.112 = 99.903

The minerals found are bronzite, olivine, nickeliferous iron, troilite, chromite, and a silicate consisting of one atom bronzite with one atom of olivine; it is opalescent, and of a greenish-yellow colour; cleaves readily. C. W. W.

The Fall of Meteorites at Gnadenfrei in Silesia, May 17th, 1879. By J. G. GALLE and A. v. LASAULX (*Jahrb. f. Min.*, 1880, 2,

Ref. 162).—The circumstances of this fall and the general characters of the two stones dug up have been already noticed in this volume (p. 237). That they are true chondrites is strikingly shown by the great abundance of spherules contained in them, many of which exhibit roundish indentations, apparently made by smaller spherules, which attached themselves to the larger ones while the mass was still in the plastic state, but were afterwards separated. The authors regard these indications as evidence that the spherules which exhibit them are fragmentary constituents of the mass. Moreover, the general impression made by an examination of the structure of the meteorites in this section is decidedly that of a conglomerate, this impression being especially produced by the fragments of spheres and hemispheres which are of not unfrequent occurrence in the mass, in many of which the edges are not sharp, but look as if they had been broken. The fragmentary character of the stone is further shown by the extraordinary brittleness of the ground-mass, in which no binding material, except perhaps metallic iron, can be detected.

Microscopical examination showed the following proximate constituents:—Nickel-iron, magnetic pyrites, troilite, chrome-iron, enstatite, olivine, and the spherules from these last two minerals.

Total Analysis.

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	Fe.	Ni.
32.11	1.60	14.88	17.03	2.01	0.70	25.16	3.92
		S.	CrO ₃ .				
		1.87	0.57	= 99.85			

with traces of P₂O₅, MnO, and Co. Sp. gr. 3.644, 3.712, 3.785.

Analysis of the silicates:—

A. *Soluble Silicate* = olivine: calc. 34.02 per cent. of the whole; found 35.01 per cent.

A1. The same calculated to 100 parts gives the formula of olivine, 2Mg₂SiO₄, Fe₂SiO₄.

B. *Insoluble Silicate* = highly ferruginous enstatite: calc. 34.03 per cent. of the whole; found 33.23 per cent.

B1. The same calculated to 100 parts gives the formula of enstatite, 3MgSiO₃, FeSiO₃.

C. Composition of the silicate reckoned as the sum of the soluble and insoluble portions.

D. Calculated composition of the silicate according to the ratio, 34.02 olivine: 34.03 enstatite.

	A.	A1.	B.	B1.	C.	D.
SiO ₂ ...	17.20	40.20	29.63	52.56	46.83	46.38
Al ₂ O ₃ ...	—	—	2.34	4.15	2.34	2.08
FeO....	12.16	28.42	9.12	16.18	21.28	22.30
MgO...	13.43	31.38	11.43	20.28	24.86	25.83
CaO....	—	—	2.83	5.02	2.83	2.51
Na ₂ O...	—	—	1.02	1.81	1.02	0.90
	42.79	100.00	56.37	100.00	99.16	100.00

The nickel-iron contains Fe = 85.1 per cent., Ni = 14.9 per cent., and its formula is Fe_8Ni .

The mass of the meteorite consists therefore of:—

Fe..... = 22.24	} Nickel-iron..... = 26.16 p. c.
Ni..... = 3.92	
Fe..... = 2.92	} Fe_8S_9 = magnetic pyrites } = 4.79 „
S..... = 1.87	
FeO.... = 0.28	} (and Troilite)
CrO ₃ = 0.57	
Enstatite = 34.03	} Chrome-iron = 0.85 „
Olivine = 34.02	
	} Silicate = 68.05 „
	99.85 „
	H. W.

Amount of Iron in the Mineral Waters of Rouen and Forges-les-Eaux. By A. HOUZEAU (*Compt. rend.*, 90, 1001).—Seven chalybeate springs at Rouen and neighbourhood were analysed.

Nos. I—III are in Rouen; No. IV at Deville-lès-Rouen; Nos. V—VII at Forges-les-Eaux.

	I.	II.	III.	IV.	V.	VI.	VII.
Matter not volatile } at 110°, grams. }	0.247	0.248	0.250	0.530	0.120	0.100	0.390
Iron, mgrs.....	22.0	13.9	7.7	5.8	3.2	7.3	43.8
Results in grams and milligrams per liter.	C. W. W.						

Crystallographic Notices. By G. SELIGMANN (*Jahrb. f. Min.*, 1880, 1, Mem. 129—150).—Phenacite, p. 129.—Antimony-glance, 135.—3. Cerussite, 137.—4. Apophyllite, 140.

Crystalline Form of Leucite. By R. WEISBACH (*ibid.*, 142—150).

Artificial Calcespar Twins, according to $-\frac{1}{2}\text{R}$. By R. BAUMHAUER (*Jahrb. f. Min.*, 1880, 1, Ref. 153).

Enargite from the Matzenköpf, near Brixlegg, in Tyrol. By V. V. ZEPHAROVICH (*ibid.*, 160).

Crystalline Forms of the Anglesites of Sardinia. By Q. SELLA (*ibid.*, 162—167).

Coquimbite. By A. ARZRUNI (*ibid.*, 167).

Boracite. By H. BAUMHAUER and E. MALLARD (*ibid.*, 168).

On the Monoclinic Form to which Epistilbite should be referred. By A. DES CLOIZEAUX (*ibid.*, 176).

Optical Orientation of Plagioclases. By M. SCHUSTER (*Jahrb. f. Min.*, 1880, 2, Ref. 8).

Crystalline Structure of Apophyllite. By J. RUMPF (*ibid.*, 11—15).

Crystallographic Examination of Norwegian Minerals: Zoisite (Thulite); Kjerulfin; Natrolite; Aeschynite; Euxenite; Polycrase (*ibid.*, 17—24).

Twin-formation and Optical Properties of Chabasite. By F. BECKE (*Jahrb. f. Min.*, 1880, 2, Ref. 135—139).

Perowskite. By H. BAUMHAUER (*ibid.*, 139—142).

Crystalline Form of Silver Iodide. By V. v. ZEPHAROVICH (*ibid.*, 142).

On the Analytical Geometric Treatment of Crystallography. By T. LIEBISCH (*Zeitschr. f. Kystallographie*, 4, 263—272; *Jahrb. f. Min.*, *ibid.*, 133).

Organic Chemistry.

Action of Chlorine and Bromine on Ethylidene Chloride and Ethyl Bromide. By TAWILDAROFF (*Bull. Soc. Chim.* [2], **34**, 346).—The action of chlorine on ethylidene chloride in presence of aluminium chloride produces trichlorethane (b. p. 114°) only. Bromine, in presence of aluminium bromide, does not act on ethyl bromide until the mixture is heated; ethylene bromide (b. p. 130°) is the sole product. In each case, the halogen attacks the methyl group, *i.e.*, the group which does not already contain halogen. J. M. H. M.

Reactions of Aluminium Chloride and Bromide with Organic Compounds. By G. GUSTAVSON (*Bull. Soc. Chim.* [2], **34**, 322—323).—The author summarises and explains these reactions as follows:—

1. Many ethereal salts combine with aluminium chloride and bromide; ethyl benzoate, for example, forms with aluminium chloride the compound $(C_6H_5.COOEt)_2.Al.Cl_6$.

2. Aluminium bromide acts on the bromine derivatives of saturated hydrocarbons with disengagement of hydrobromic acid, and in some cases the formation of a saturated hydrocarbon. Compounds of aluminium chloride with an unsaturated hydrocarbon are produced at the same time. By the action of aluminium bromide on ethyl bromide, for example, the compound $Al_2Br_6.C_8H_{16}$ is produced, with disengagement of hydrobromic acid.

3. Reactions similar to that of bromine on benzene, isobutyl bromide, ethylidene chloride, and the saturated petroleum hydrocarbons, in presence of a small quantity of aluminium bromide. These reactions result in substitution of bromine, and depend on the repeated displacement of Al_2Br_6 (by bromine) from its combination with the unsaturated hydrocarbon derivatives. In the first two cases, the quantity of the product is proportional to that of the aluminium chloride or bromide employed; in the last case, a small quantity of aluminium

compound determines the transformation of an indefinite quantity of the original compound into new products. J. M. H. M.

Action of Alcoholic Bromides and of Hexabromethane in presence of Aluminium Bromide on the Paraffins extracted from the Lowest-boiling portions of Petroleum. By G. GUSTAVSON (*Bull. Soc. Chim.* [2], 34, 325).—These reactions result in the disengagement of hydrobromic acid and the formation of two layers of liquid, the lower of which contains compounds of aluminium bromide with the new hydrocarbons produced. The action of aluminium bromide on the petroleum hydrocarbons is especially remarkable. All the bromine of the hexabromethane is evolved as hydrobromic acid at the ordinary temperature. Acetic bromide also reacts with these hydrocarbons in presence of aluminium bromide. J. M. H. M.

Boiling Points of Ethylene and Ethane Derivatives. By SABANÉEFF (*Bull. Soc. Chim.* [2], 34, 323).—The differences between the boiling points of analogous halogen derivatives of ethane and ethylene are constant, being determined by the nature of the halogen and not by its amount. For the chlorine derivatives, the constant difference is about 30° , for the bromine derivatives 23° , and for the iodine derivatives 16° . In proof, the author cites the following instances:—

	B. p.	Diff.
$\text{CH}_3\cdot\text{CH}_2\text{Cl}$	12°	} $29-30^\circ$
$\text{CH}_2:\text{CHCl}$ - 17° to	-18°	
$\text{CH}_2\text{Cl}\cdot\text{CHCl}_2$	115°	} 28°
$\text{CHCl}\cdot\text{CCl}_2$	87°	
	B. p.	Diff.
$\text{CH}_3\cdot\text{CHBr}_2$	$110-112^\circ$	} $22-24^\circ$
$\text{CH}_2:\text{CBr}_2$	88°	
$\text{CH}_3\cdot\text{CHI}$	72	} 16
$\text{CH}_2:\text{CHI}$	56	

J. M. H. M.

Hexmethylethane. By O. Lwow (*Bull. Soc. Chim.* [2], 35, 169).—By the action of sodium on an ethereal solution of tertiary butyl iodide, hexamethylethane, C_2Me_6 , is obtained. It melts at $96-97^\circ$, boils at $105-106^\circ$, and sublimes readily. L. T. O'S.

Hydrocarbons obtained as Bye-products in the Decomposition of Levulic Acid by Hydriodic Acid. By E. A. KEHRER and B. TOLLENS (*Annalen*, 206, 248—250).—In addition to the valeric acid formed by the action of hydriodic acid on levulic acid (*see* p. 411), the authors find that there is an oily substance, which, on fractionating, separates into two portions: one boiling at $130-160^\circ$, and the other at $200-265^\circ$. From the results of the analyses, it is impossible to definitely assign any formulæ to the substances. They appear to contain small quantities of unsaturated hydrocarbons. J. I. W.

Chlorine Tetroxide and Ethylene. By E. FÜRST (*Liebig's Annalen*, 206, 78—82).—In the dark, a mixture of chlorine tetroxide

and ethylene remains unaltered, but quickly becomes colourless in diffused daylight, with the formation of oily drops, which solidify over sulphuric acid. Their solution is acid, and after careful neutralisation with calcium carbonate, yields crystals of *calcium glycolate*. This is formed by the decomposition of *monochloroacetic acid*, which, in its turn, is derived from *monochloroacetic chloride*, the primary product of the reaction of the gases: $2\text{ClO}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_2\text{ClOCl} + \text{H}_2\text{O} + \text{O}_2$.

O. H.

Polymerisation of Vinyl Bromide. By O. LWOW (*Bull. Soc. Chim.* [2], 35, 169—170).—The chlorinated and brominated hydrocarbons do not prevent the polymerisation of vinyl bromide under the action of light, but it is completely arrested by the presence of methyl or ethyl iodide, which is decomposed with liberation of iodine. If vinyl bromide contains sufficient iodine to colour it violet, the polymerisation ceases until, under the influence of the sun's rays, the colour disappears. A slight excess of iodine, however, completely stops the polymerisation in the liquid; but the vapours of vinyl bromide above the liquid slowly become polymerised. Aniline also arrests polymerisation, but it is greatly increased by sulphurous anhydride. Air and water have no influence, but carbonic anhydride slightly hinders the action of light.

L. T. O'S.

Atomic Migration. By ELTÉKOFF (*Bull. Soc. Chim.* [2], 34, 347).—The author finds that when isobutyl iodide is heated with lead oxide, pseudobutylene (symmetrical dimethylethylene) is formed, besides isobutylene, thus confirming Kononoff's observation (next Abstract). The general conclusion arrived at by the author in connection with this subject is, that the isomerisation of a given hydrocarbon of the ethylenic series does not tend exclusively to the accumulation of methyl groups, as has been hitherto believed, but rather to the greatest possible symmetry of the substituted ethylene molecule.

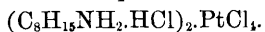
J. M. H. M.

Isobutylene. By KONOVALOFF (*Bull. Soc. Chim.* [2], 34, 333—334).—The butylene obtained by the action of sulphuric acid on isobutyl alcohol is not homogeneous, about two-thirds being isobutylene; whilst the remainder consists of pseudobutylene and a small quantity of a saturated hydrocarbon boiling below -10° , probably trimethylmethane. The pseudobutylene (symmetrical dimethylethylene) remains unattacked when liquefied and heated in sealed tubes with 2 parts sulphuric acid and 1 of water. The isobutyl alcohol employed contained no other variety of butyl alcohol, and when converted into butyl iodide and heated with potash, yielded over 90 per cent. of the theoretical amount of isobutylene.

J. M. H. M.

Action of Nitric Acid on Isodibutylene. By KONOVALOFF (*Bull. Soc. Chim.* [2], 34, 334).—Isodibutylene (b. p. $102-104^\circ$) treated with nitric acid (sp. gr. 1.28) in a flask with an inverted condenser, furnishes a clear green liquid of penetrating odour, heavier than water, and giving an orange-red colour to an aqueous solution of soda. When treated with tin and hydrochloric acid, this liquid yields a considerable quantity of an oily organic base, scarcely soluble in water,

and with a strong alkaline reaction. It absorbs carbonic anhydride from the air, forming a crystalline carbonate. Its salts are unstable, and crystallise with difficulty. The base itself is partially decomposed by distillation. The chloroplatinate has the formula



J. M. H. M.

Cholestene (Cholesterilene). By W. E. WALITZKY (*Compt. rend.*, **92**, 195—196).—By the prolonged action of sodium on cholesterin fused at $150\text{--}155^\circ$, the author obtained the hydrocarbon $\text{C}_{26}\text{H}_{42}$. It is an amorphous, slightly yellow powder, soluble in ether, but almost insoluble in alcohol, which precipitates it from the ethereal solution. With bromine it forms a compound having the composition $\text{C}_{26}\text{H}_{34}\text{Br}_8$, and in all its physical and chemical properties closely resembles both the "*c-cholesterilene*" obtained by Zwenger by the action of sulphuric acid on cholesterin, and also the cholestene obtained by the author by treating cholesterin with concentrated hydriodic acid. The same hydrocarbon appears to be formed when cholesterin is heated with zinc, or with soda-lime or potash-lime.

C. H. B.

Nitroprussides of the Alkaloids. By E. W. DAVY (*Pharm. J. Trans.* [3], **11**, 756—757).—On adding sodium nitroprusside to solutions of the alkaloids, amorphous precipitates or oily drops separate out, which on standing present a crystalline appearance. In the case of morphine and nicotine, the salts are soluble in water, they are therefore prepared by treating the hydrochloride of the alkaloids with silver nitroprusside, or by the direct union of the base and acid. In some cases both neutral and acid salts exist, but in the case of morphine, strychnine, and brucine, all attempts to prepare the acid salts have failed.

The salts of brucine, strychnine, and quinine are very sparingly soluble in water, dissolving in 736, 847, and 2,500 times their weight of water respectively.

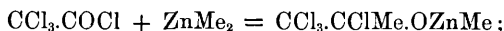
L. T. O'S.

Formation of a Secondary Alcohol. By STCHERBAKOFF (*Bull. Soc. Chim.* [2], **34**, 347).—By the action of water on the compound of normal butyric chloride with zinc-propyl, the author has obtained dipropylcarbinol. This is an instance of the formation of a secondary alcohol by a reaction hitherto recognised as affording tertiary alcohols only.

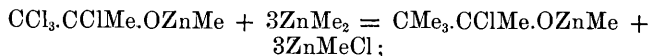
J. M. H. M.

Action of Zinc Methide on Chloracetic Chlorides. By BOGOMOLETZ (*Bull. Soc. Chim.* [2], **34**, 330—332).—The action of zinc methide on monochloracetic chloride (b. p. $105\text{--}107^\circ$) gives rise to methylisopropyl carbinol, the secondary amyl alcohol prepared by Winogradoff by the action of zinc methide on monobromacetic bromide. By the action of zinc methide on dichloracetic chloride (b. p. 108°), and trichloracetic chloride (b. p. $116\text{--}118^\circ$), tertiary alcohols are produced; dimethylisopropyl carbinol (6 per cent. of the theoretical yield) in the former case, and pentamethylethol, the heptylic alcohol of Butlerow (40 per cent. of the theoretical yield), in the latter. The

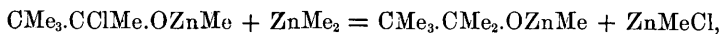
author considers that there is at first a combination of zinc methide with the polychloroacetic chloride:—



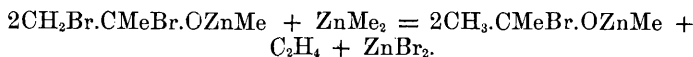
then a replacement of chlorine by methyl in the group CCl_3 —



finally the chlorine in the group COCl is replaced—



and $\text{CMe}_3.\text{CMe}_2.\text{OZnMe} + 2\text{H}_2\text{O} = \text{CMe}_3.\text{CMe}_2.\text{OH} + \text{CH}_4 + \text{Zn}(\text{OH})_2$. The formation of acetone by the action of zinc methyl on monobromoacetic bromide is explained in a similar manner, the following equation representing the second stage in the reaction:—



J. M. H. M.

Allylmethylpropylcarbinol and β -Methylpropylethylenelactic Acid. By A. SEMLJANITZIN (*J. pr. Chem.* [2], **23**, 263—269).—Allylmethylpropylcarbinol is prepared by slowly pouring a mixture of allyl iodide and methylpropylketone on metallic zinc, contained in a well-cooled retort, which is connected with a condenser. After leaving the mixture at rest for several hours, water is added, and the product distilled. The oily distillate is then dried and fractionated. The pure carbinol is a colourless liquid, which has no action on a ray of polarised light. It boils at 159° , has a sp. gr. of 0.5488 at 0° , and a coefficient of expansion of 0.00084 for 1° . It is insoluble in water. On oxidation with potassium permanganate, or a mixture of dilute sulphuric acid and potassium dichromate, it yields methylpropylketone and *methylpropylethylenelactic acid*, $\text{CMePr}(\text{OH}).\text{CH}_2.\text{COOH}$. This acid is an uncrystallisable syrup. The *calcium* and *barium* salts were obtained as crystalline crusts, and the *silver salt*, $\text{C}_7\text{H}_{13}\text{O}_3\text{Ag}$, was deposited from a hot aqueous solution in short prisms. W. C. W.

Oxidation of Erythrol and Glycerol. By PRZYBYTEK (*Bull. Soc. Chim.* [2], **35**, 108—109).—Erythrol, when oxidised with nitric acid, yields oxalic and tartaric acids; also a large quantity of hydrocyanic acid. With potassium permanganate and chromic acid, or chromic mixture, carbonic anhydride, formic, and oxalic acids were formed.

Glycerol, when treated with nitric acid, yields large quantities of hydrocyanic acid and racemic acid, which is formed by the synthetic action of the hydrocyanic acid on one of the products of oxidation, possessing the properties of an aldehyde, $\text{CHO}.\text{CHO}$, or perhaps $\text{CHO}.\text{CH}(\text{OH}).\text{CHO}$, and not by a combination of 4 atoms of carbon, as Heintz suggests. L. T. O'S.

Preparation of Sucrose from Glucose. By COLLEY and VAKOVITCH (*Bull. Soc. Chim.* [2], **34**, 326—327).—When l  vulosate of sodium, obtained by precipitating sodium ethylate with an alcoholic

solution of lævulose, is treated with acetochlorhydrose (a derivative of dextrose), sodium chloride is formed, and a substance which is probably the tetracetic salt of an isomeride of sucrose. When this ethereal salt is decomposed by baryta, it gives a solution which turns the plane of polarisation 8° to the left. After ebullition with hydrochloric acid, the optical activity of the solution is -5° . The action of acetochlorhydrose on dextrosate of sodium also gives a product which is capable of inversion. The isomeride of sucrose supposed to be formed in these experiments is therefore lævorotatory. By the action of acetochlorhydrose on a concentrated alcoholic solution of lævulose, in presence of barium carbonate, a product is formed (with disengagement of carbonic anhydride and formation of barium chloride) which rotates the plane of polarisation 2° to the right, and after inversion 1.5° to the left. This substance is perhaps ordinary sucrose.

J. M. H. M.

Gelose. By H. MORIN (*Compt. rend.*, **90**, 924).—This substance, which is remarkable for forming a jelly with 500 times its weight of water, was first studied by Payen (*Compt. rend.*, 1859, 521). It has since been introduced into commerce in considerable quantities, under the names of China-moss (*mousse de Chine*), and Ta-ô; it is used in making jellies, and for the preparation of certain stuffs.

It is oxidised by dilute nitric acid, with formation of mucic and oxalic acids. Dilute mineral acids, also acetic and oxalic acids, deprive it of its property of gelatinising; water heated until at a pressure of 5—6 atmospheres has a similar effect.

The air-dried substance loses 22.85 per cent. of water at 100° , and leaves 3.88 per cent. of ash when burnt.

A 10 per cent. aqueous solution has a lævogyrotory power for a yellow light of $-4^\circ 15'$; by the continued action of acidulated water this is converted into a nearly equal dextrorotatory power. This dextrogyrate solution reduces cupropotassic solution, and also mercuric chloride and auric chloride.

Alcohol precipitates the lævogyrate solution, but the precipitate contains a larger proportion of ash than the original substance.

All these properties seem to ally gelose with the gums.

C. W. W.

Gelose. By PORUMBARU (*Compt. rend.*, **90**, 1081).—The formula of pure gelose is $C_6H_{10}O_6$, analogous to the formulæ of lichenin, inulin, and tunisin.

The action of water on gelose at temperatures from 100° to 150° , gives rise first to one or more products reducing cupropotassic solution and having a lævorotatory action, and finally to a brown ulmic substance. The lævorotatory substance has the formula $C_6H_{12}O_6 + H_2O$.

A one per cent. solution of sulphuric acid at 100° gives rise to another substance reducing cupropotassic solution, and crystallising from alcohol in long needles. These results differ in several particulars from those obtained by Morin (see above).

C. W. W.

Multiples in the Rotatory Powers of Organic Compounds. By H. LANDOLT (*Ber.*, **14**, 296—299).—This is a critical examination

of the conclusions of T. Thomsen (*Ber.*, **13**, 2168, 2264, 2266, 2269; and **14**, 29, 134, 158, and 205). The author regards the law of T. Thomsen as without foundation, and of no value, and is of the opinion that the materials resulting from observations on this subject are still insufficient for generalisations of this character.

P. P. B.

Methyl and Ethyl Ethers of Diallylcarbinol. By K. RJABININ (*J. pr. Chem.* [2], **23**, 269—276).—The methyl ether of diallylcarbinol, $C_7H_{11}.OCH_3$, is formed when the sodium compound of diallylcarbinol is heated with an excess of methyl iodide. After distillation over sodium, the ether boils at 135° , and has a sp. gr. of 0.8258 at 0° , and its coefficient of dilatation equals 0.0010 for 1° . It combines directly with 4 atoms of bromine. On treating the ether with potassium permanganate, oxidation takes place at the double linking of the carbon atoms, β -methoxyglutaric acid, $OMe.CH(CH_2.COOH)_2$, being formed, together with oxalic acid. β -Methoxyglutaric acid is a syrupy liquid, crystallisable with difficulty. The silver salt, $C_6H_8Ag_2O_5$, forms small prismatic crystals. The ethylic ether of diallylcarbinol, $C_7H_{11}.OEt$, boils at 143° , and has a sp. gr. of 0.8218 at 0° . It combines directly with 4 atoms of bromine. Attempts to prepare an acid having the composition $OEt.CH(CH_2.COOH)_2$ by the oxidation of this ether were unsuccessful.

W. C. W.

Action of Hydrochloric Acid on Aldehyde. By HANRIOT (*Compt. rend.*, **92**, 302—303).—By the action of hydrochloric acid on aldehyde, Lieben obtained a compound, $C_4H_8OCl_2$, to which he gave the name ethylidene oxychloride. Geuther and Cartmell supposed the existence of an intermediate product, $C_6H_{12}Cl_2O_2$. The author has found that when a slow current of dry hydrochloric acid gas is passed into aldehyde, carefully cooled, the latter can absorb half its weight of the gas without becoming turbid, and a liquid is obtained which boils at 25° under a pressure of 0.04 m., and has the composition $C_4H_8O_2.2HCl$. This body readily loses water under the influence of an excess of hydrochloric acid, or of heat, or even when left to itself after purification, giving Lieben's compound, $C_4H_8OCl_2$.

If a rapid current of hydrochloric acid gas is passed into aldehyde, cooled to 0° , water separates out, and the upper layer of liquid when distilled boils at 58 — 60° under a pressure of 0.04 m. It consists mainly of $C_4H_8OCl_2$, but contains a small quantity of another liquid which passes over at 100° , and has the composition $C_6H_{12}OCl_2$. This compound is decomposed by water with formation of crotonaldehyde, and is probably analogous to ethylene oxychloride. The quantity formed is greater the longer the passage of the acid gas is continued, but the yield is always very small.

From the method of its formation, ethylidene oxychloride appears to be symmetrical dichlorinated ether, $CHMeCl.O.CHMeCl$. It combines readily with alcohol, forming ethylidene acetochlorhydrin, and is decomposed very slowly by cold, more rapidly by boiling water, giving hydrochloric acid and aldehyde.

When a current of ammonia gas is passed into an ethereal solution of the ethylidene oxychloride, long needles rapidly separate out.

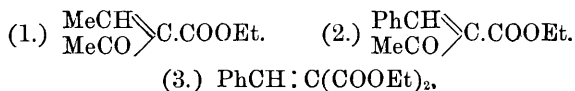
They have the composition $\text{CHMeNH}_2 \cdot \text{O} \cdot \text{CHMeNH}_2 \cdot 2\text{HCl}$, and effloresce rapidly in dry air, losing a portion of their hydrochloric acid; their aqueous solution rapidly decomposes, and when heated on platinum foil the crystals give off a pyridic odour. C. H. B.

Condensation of Aldehydes with Ethyl Acetate and Malonate. By L. CLAISEN (*Ber.*, 14, 345—349. First Notice).—A mixture of molecular quantities of acetaldehyde and ethyl acetate absorbs hydrochloric acid gas in the cold: the product, after standing 12—24 hours, is poured into cold water, when an oil separates out which, after washing with soda and drying over calcium chloride, is distilled. The colourless liquid, $\text{C}_8\text{H}_{12}\text{O}_3$, thus obtained boils at $210\text{--}212^\circ$, is heavier than water, and insoluble in it. It takes up a molecule of bromine, forming a dibromide, a yellow thick oil, and decomposed by distillation. The dibromide dissolves in potash; by acidifying the solution the acid, of which the above is the ethyl salt, is obtained as an uncrystallisable syrup.

Benzaldehyde and ethyl acetate, when treated in a similar manner, yields a liquid which boils between $180\text{--}183^\circ$ under a pressure of 17 mm. (under ordinary pressure it boils at $295\text{--}297^\circ$, and is partially decomposed). It is a pale yellow, thick, strongly refractive oil, possessing but a weak odour, and having the composition $\text{C}_{13}\text{H}_{14}\text{O}_3$. With bromine, it forms a dibromide, which is largely soluble in chloroform, benzene, and ether, and sparingly in alcohol and light petroleum, from which it crystallises in fine prisms (m. p. 97°).

Benzaldehyde and ethyl malonate also yield a condensation-product of the composition $\text{C}_{14}\text{H}_{16}\text{O}_4$; it is a liquid which boils at 190° to 193° under a pressure of 17 mm.

From this it would appear that benzaldehyde and acetaldehyde behave in a similar manner, and also that ethyl acetate and malonate behave similarly to one another, hence the author attributes the following constitutional formulæ to the above:—



(1) is styled ethylic acetethylidene-acetate, (2) ethylic acetobenzylidene-acetate, and (3) ethylic benzylidene-malonate. P. P. B.

Preparation of Crotonaldehyde. By NEWBURY (*Compt. rend.*, 92, 196—198).—Crotonaldehyde may be readily obtained by Wurtz's method. This consists in preparing aldol by the action of hydrochloric acid on aldehyde or paraldehyde, and subsequent distillation of the aldol formed. 2 parts hydrochloric acid, 1 part water, and 1 part aldehyde or paraldehyde are mixed and kept at about 25° for four or five days. If aldehyde is used, the liquid should be kept at zero whilst the acid is added, otherwise the aldehyde is transformed immediately into paraldehyde. To ascertain the progress of the reaction, a small quantity of the liquid is from time to time neutralised with sodium carbonate, and the quantity of resin which separates out is observed.

The best yield of aldol is obtained when this resin forms a thick, oily non-crystalline layer. The liquid is then neutralised with sodium carbonate, allowed to stand several hours, the precipitated dialdane filtered off, and the filtrate agitated several times with ether. The ether is then distilled off on the water-bath, and the aldol is separated from the residual oily liquid by distillation under reduced pressure. Aldol sufficiently pure for the preparation of crotonaldehyde, passes over between 85° and 120° under a pressure of 0.2 m. About 500 grams of impure aldol may in this way be obtained from 1 kilo. of aldehyde or paraldehyde. Crotonaldehyde is obtained from the impure aldol, either by heating 2 parts of the latter with 1 part of water under pressure at 150° for one hour, or better, by distilling the aldol in a retort with an inverted neck connected with a condenser. The crotonaldehyde is separated from the water which passes over along with it, and dried by means of calcium chloride. When carefully purified it boils at $103\text{--}104^{\circ}$. By this process, 100—125 grams crotonaldehyde may be obtained from 1 kilo. of aldehyde or paraldehyde.

C. H. B.

Derivatives of Acrolein. By E. GRIMAUX and P. ADAM (*Compt. rend.*, **92**, 300—302).—By the action of hydrochloric acid gas on acrolein, Geuther and Cartmell obtained an addition-product, acrolein hydrochloride, and this by loss of hydrochloric acid gave metacrolein, a solid polymeride of acrolein. Krestownikoff showed that this hydrochloride could be transformed into β -chloropropaldehyde.

Para-chloropropaldehyde may be readily obtained by passing dry hydrochloric acid gas into acrolein kept cool by means of a freezing mixture. It forms large transparent needles, resembling the crystals of sodium sulphate. These melt at 33.5° and distil at $170\text{--}175^{\circ}$ under a pressure of 12—15 mm., crystallising immediately in the receiver. When distilled under ordinary pressure, traces of hydrochloric acid and acrolein are given off, and at $130\text{--}170^{\circ}$ there passes over depolymerised chloropropaldehyde, which however is soon converted into the polymeric modification owing to the presence of small quantities of hydrochloric acid. *Para-chloropropaldehyde*, like paraldehyde and paraisobutaldehyde, and unlike chloropropaldehyde, does not reduce an alkaline solution of copper oxide. It is a very stable body, and is not acted on by water or baryta at 100° , or by silver or lead acetates at 120° : the chlorine may be replaced by the group OH. At 110° , water and baryta set free hydrochloric acid, but the greater part of the compound is converted into a resin analogous to di-acryl. Sodium ethylate acts on it readily, giving an oily liquid, which has not yet been examined.

Metacrolein was obtained by distilling the *para-chloropropaldehyde* with its own weight of powdered potash (Geuther and Cartmell): the yield was only small. It crystallises from its solution in alcohol in beautiful transparent plates (m. p. $45\text{--}46^{\circ}$). Its vapour-density at 132° , by Hofmann's method, is 5.9 (air = 1), and its formula is $C_9H_{12}O_3 = 3C_3H_4O$. At 160° , it begins to dissociate. *Meta-crolein*, dissolved in chloroform, combines directly with bromine, giving a compound which crystallises in small nacreous needles, and

is identical with the substance obtained by Henry and Lippemann by the polymerisation of acrolein bromide. Its formula is $C_9H_{12}Br_2O_3 = 3C_3H_4Br_2O$. The formula of para-chloropropaldehyde is in all probability $C_9H_{12}Cl_3O_3 = 3C_3H_4ClO$. C. H. B.

Dichloraldehyde Hydrate. By R. FRIEDRICH (*Annalen*, **206**, 251—254).—In the preparation of butyl chloride from paraldehyde and chlorine by Pinner's method, there is formed a small quantity of a substance which boils at 98—100°. On standing for a month, the author finds that it deposits monoclinic crystals. These should consist of chloral hydrate melting at 57°; but they melt at 43°. The author finds that the substance is dichloraldehyde hydrate, $C_2Cl_2O_2H_4$, as it can be converted into dichloroacetic acid and dichloraldehyde. When pure it dissolves easily in water, ether, and carbon bisulphide: from benzene, it separates in good monoclinic crystals. The dichloraldehyde obtained from it is an amorphous paraffin-like mass (m. p. 200°).

J. I. W.

Dissociation of Butylchloral Hydrate. By ENGEL and MOITESIER (*Compt. rend.*, **90**, 1075).—Kramer and Pinner (*Annalen*, **158**, 37) found the vapour-density of butylchloral hydrate to be about the fourth of the theoretical density; they considered therefore that the molecule was probably broken up into water, carbonic oxide, hydrochloric acid, and dichlorallylene.

The authors have arrived at a different result. They find that the vapour-density of the compound, taken by Hofmann's method in vapour of turpentine, is 3.328 (air = 1). Theory for 2 vols. = 6.7. The density found corresponds, therefore, to 4 vols.; and since the butylchloral hydrate is deposited unchanged on cooling, it is evident that there can have been no decomposition of the butylchloral.

The dissociation of the hydrate is rendered evident by the following facts:—

It has no fixed boiling point. When heated, it begins to distil at 100°, the temperature rises rapidly and remains fixed at 165°, when the distillate is anhydrous butylchloral. The tension of the vapour of butylchloral hydrate at 100° is greater than the atmospheric pressure (about 860 mm.). When it is distilled with chloroform, the water is entirely separated. When the hydrate is heated rather above its melting point, it gradually separates into two layers, the lower of which is a saturated aqueous solution of butylchloral hydrate, the upper being anhydrous butylchloral. Finally, butylchloral hydrate is no longer volatile in presence of the vapour of one of the products of its decomposition at a tension superior to the dissociation-tension of the compound at the same temperature.

The last law is of general application.

C. W. W.

Action of Aluminium Chloride on Acetic Chloride. By WINOGRADOFF (*Bull. Soc. Chim.* [2], **34**, 325).—The reaction takes place at 30—40°, in conformity with the equation $Al_2Cl_6 + 4C_2H_3OCl = 4HCl + 2(AlCl_3.C_4H_4O_2)$. The solid product, $CH_3.CO.CH:CO.AlCl_3$, is decomposed by water with disengagement of carbonic anhydride and formation of acetone.

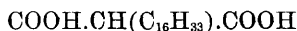
J. M. H. M.

Dry Distillation of Potassium Dichloracetate. By R. FREIDRICH (*Annalen*, **206**, 244—256).—The author finds that when potassium dichloracetate is subjected to dry distillation, the residue consists merely of potassium chloride and carbon, and the distillate contains dichloroacetic acid. The decomposition appears to occur in the following manner: $2\text{CHCl}_2.\text{COOK} = 2\text{KCl} + \text{CHCl}_2.\text{COOH} + \text{C} + \text{CO}_2$. Kekulé found (*Annalen*, **105**, 286) that potassium monochloracetate gives by dry distillation potassium chloride, glycollic acid, and glycolide. It was to be expected that potassium dichloracetate would give a chlorinated glycolide. J. I. W.

Triacetin. By KABLOUKOFF (*Bull. Soc. Chim.* [2], **34**, 347—348).—In order to obtain a triatomic alcohol with 6 carbon-atoms, the author reduced allylacetone, $\text{C}_3\text{H}_5.\text{CH}_2.\text{CO}.\text{CH}_3$, into an alcohol, and thence into an acetate. From the acetate he prepared acetobromhydrin, $\text{AcO}.\text{CHMe}.\text{CH}_2.\text{C}_3\text{H}_5\text{Br}_2$, which, when heated with silver acetate, yielded triacetin, $\text{C}_6\text{H}_{11}(\text{OAc})_3$, boiling without decomposition under the ordinary atmospheric pressure. J. M. H. M.

Calcium and Barium Salts of Diethyl- and Methyl-propyl-acetic Acids. By A. SAYTZEFF (*J. pr. Chem.* [2], **23**, 288—297).—A re-examination of the calcium and barium diethylacetates shows that the hydroethylcrotonic acid of Howe and Fittig (*Annalen*, **200**, 24) is identical with the diethylacetic acid which the author obtained from the cyanide of diethyl carbinol (*ibid.*, **193**, 349). The discrepancy observed in the solubility of the calcium salts from the two sources, is attributed to the presence of a small quantity of calcium ethyl crotonate in Fittig's preparation. The author has again examined calcium and barium methylpropylacetates, and confirms the accuracy of his previous description of their properties. W. C. W.

Cetyl- and Dicetyl-acetic and -malonic Acids. By M. GUTHZEIT (*Annalen*, **206**, 351—367).—*Cetyl-malonic acid* is prepared by saponification of ethylic cetylmalonate, obtained by the action of sodium ethylate on cetyl iodide and ethyl malonate. On decomposing its calcium salt with hydrochloric acid, the acid



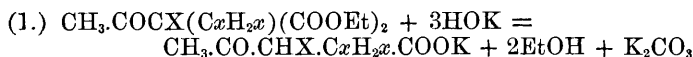
is obtained in the pure state as a colourless crystalline mass (m. p. 117°). The acid is soluble in ether and hot alcohol, but separates out from the latter on cooling; the silver salt forms a voluminous white precipitate.

Cetyl-acetic acid may be prepared by the action of potash on ethylic cetyl aceto-acetate, thus: $\text{CH}_3\text{CO}.\text{CH}(\text{C}_{16}\text{H}_{33}).\text{COOEt} + 2\text{KOH} = \text{CH}_3\text{COOK} + \text{CH}_2(\text{C}_{16}\text{H}_{33}).\text{COOK} + \text{EtOH}$. But a more practical method is by the action of baryta-water on cetylmalonic acid. The acid forms a crystalline warty mass (m. p. 63.5°), soluble in ether, insoluble in water and absolute alcohol. It is distinguished in its melting point from its isomerides, dioctylacetic acid (m. p. 38.5°) and stearic acid (m. p. $69-70^\circ$). The silver salt forms a voluminous flocculent white precipitate.

Dicetylmalonic acid is prepared by the action of sodium ethylate on a mixture of ethyl malonate with cetyl iodide and subsequent saponification of the ethyl salt with potash. The acid may be obtained by decomposing the sparingly soluble calcium salt with hydrochloric acid. The acid forms small crystals (m. p. 86—87°), insoluble in cold but soluble in hot alcohol. The silver salt forms a flocculent white precipitate.

Dicetylacetic acid is prepared by the action of baryta-water on dicetylmalonic acid. It separates out from absolute alcohol as an amorphous precipitate (m. p. 69—70°). The silver salt is amorphous, not decomposed by light. V. H. V.

Decomposition of Polybasic Aceto-acetates by Alkalis. By J. WISLICENUS (*Annalen*, 206, 308—313).—The author has established that alcoholic aceto-acetates are decomposed by alkalis into carbonic acid and a ketone, or into acetic and a second monobasic acid, according as the alkali is dilute or concentrated (*Annalen*, 190, 257). Subsequently, the author studied a similar reaction with dibasic aceto-acids, and found that these are decomposed into carbonic and a ketonic acid, or into acetic and a dibasic acid, thus:—



By determining the amount of potash converted into carbonate, and that converted into the potassium salts of the acids, the amount of decomposition accorded to either equation is established.

The author has investigated this reaction with the ethereal salts of aceto-succinic, α - and β -methylaceto-succinic, α - and β -ethylaceto-succinic, aceto-glutaric, and α -methylaceto-glutaric acid. From the tables in the paper, it follows:—(1.) That the more dilute the alkali, the greater the quantity of carbonate, and the stronger the alkali, the greater the quantity of acetic and dibasic acid formed. (2.) In isomeric acids the relative quantity of each decomposition is not equal. The α -acid gives less carbonic and ketonic, but more acetic and dibasic acids than the corresponding β -acid. The ethereal salts of an aceto-tricarballic acid corresponding to the above α -acids give no carbonate, but only acetic and tricarballic acid. V. H. V.

Preparation and Properties of Levulic or β -Acetopropionic Acid. By A. F. GROTE, E. KEHRER, and B. TOLLENS (*Annalen*, 206, 207—225).—The authors find that levulic acid, $\text{C}_5\text{H}_8\text{O}_3$, is best prepared in the following manner. A mixture of 15 parts of white "crystalline sugar," 15 parts of water, and 1 part of concentrated sulphuric acid is heated for two days in the water-bath, with an inverted condenser. It is then separated from the humus substance by pressure, and the filtrate is again heated for two days. After filtration, the liquid is treated with calcium carbonate: the calcium salt so formed is next decomposed by sulphuric acid, and the levulic acid

separated by extracting with ether, and fractionally distilling. In order to obtain the acid quite pure, the calcium salt is decomposed by the calculated amount of oxalic acid. It melts at $31-31.66^{\circ}$, and boils at 239° . It forms rhombic crystals, with angles about 41.5° and 142.5° . The authors find that by employing hydrochloric acid instead of sulphuric acid in its preparation, the yield of the acid, as Conrad has pointed out (*Ber.*, **11**, 2178), is greater, but the product is not so pure. From 500 grams of sugar, hydrochloric acid gives 35.6 grams of levulic acid; sulphuric acid gives 31.5 grams. The *calcium salt*, $(C_6H_7O_3)_2Ca + 2H_2O$, is obtained by neutralising the acid with calcium carbonate. It crystallises in needles, which lose their water of crystallisation at $140-150^{\circ}$. The authors state that the monohydrated calcium salt mentioned by Grote and Tollens appears to have no existence. The *silver salt*, $C_6H_7O_3Ag$, is best prepared by decomposing the zinc salt with silver nitrate. After repeated boiling with animal charcoal, it is obtained in crystalline plates. The *sodium salt*, $C_6H_7O_3Na$, is prepared by acting on the calcium salt with sodium carbonate. It crystallises in cauliflower-like masses, composed of small needles, which are deliquescent. The *copper salt*, $(C_6H_7O_3)_2Cu$, forms bluish-green crystals. The *barium salt* forms a gum-like mass, which will not crystallise. The *magnesium salt* is similar to the barium salt. The *nickel salt* forms bright green needles.

The *methyl salt of levulic acid*, $C_6H_7O_3Me$, is formed when the silver salt is heated with the theoretical quantity of methyl iodide in a sealed tube at 100° for 24 hours. The pure ether boils at $191-191.5^{\circ}$ at 743 mm. Its sp. gr. at 0° is 1.0684, at 20° , 1.0519. Its refractive index for D is 1.4240.

The *ethyl salt*, $C_6H_7O_3Et$, is obtained by passing a stream of hydrochloric acid gas into a warm alcoholic solution of the acid. It boils at $200-201^{\circ}$ at 756 mm. (corr. 205.2). Its sp. gr. at 0° is 1.0325, at 20° , 1.0156. Its vapour-density is 71.4 (cal. = 72). Its refractive index for D is 1.4234.

The *propyl salt*, $C_6H_7O_3Pr$, prepared by heating the silver salt with propyl iodide, boils at $215-216^{\circ}$ (uncorr.). It has a melon-like smell and a burning taste. Its sp. gr. at 0° is 1.0103, at 20° , 0.9937. Its refractive index for D is 1.4270.

The physical properties of the free acid and of its ethers show that its formula is identical with that of β -acetopropionic acid.

J. I. W.

Formation of Levulic Acid from Dextrose. By A. v. GROTE and B. TOLLENS (*Annalen*, **206**, 226-231).—The authors find that if pure dextrose be heated with sulphuric or hydrochloric acid, preferably the latter, it yields small quantities of levulic acid.

J. I. W.

Formation of Levulic Acid from Milk-sugar. By H. RODEWALD and B. TOLLENS (*Annalen*, **206**, 231-232).—The authors find that as cane-sugar yields inulin and other carbohydrates, so milk-sugar gives levulic acid. In addition to the levulic acid, a small quantity of formic acid is produced.

J. I. W.

Conversion of Levulic Acid into Normal Valeric Acid.

By E. A. KEHRER and B. TOLLENS (*Annalen*, **206**, 233—248).—The authors find that if levulic acid is treated with hydriodic acid, it yields normal valeric acid. This shows that levulic acid contains only singly combined carbon atoms. The valeric acid is formed according to the equation $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH} + 4\text{HI} = \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH} + \text{H}_2\text{O} + 4\text{I}$. The authors heat 5 parts of levulic acid with 20 parts of hydriodic acid of sp. gr. 1.96, and 1 part of red phosphorus for 12 hours at 150° . The contents of the tubes are neutralised with sodium carbonate, and the sodium salt is decomposed by sulphuric acid. The free acid is purified by distillation. When pure it boils at 185.75° (corr.). Its sp. gr. at 0° is 0.9608, at 20° it is 0.9448. The acid has an odour similar to that of butyric acid.

Ethyl salt of valeric acid, $\text{C}_5\text{H}_9\text{O}_2\text{Et}$, is prepared by passing hydrochloric acid gas into an alcoholic solution of valeric acid until it is saturated, and then heating the liquid in a sealed tube at 100° . It boils at 144.5° . Its refractive index for D at 17.5° is 1.4067. This gives 60.1 for the molecular refraction, whilst, calculating the theoretical value from Landolt and Brühl's numbers, 59.4 is obtained.

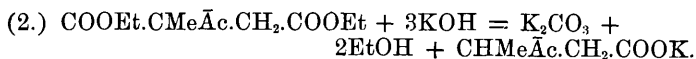
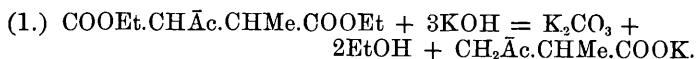
The authors prepared *barium valerate*, $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ba}$, and *calcium valerate*, $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ca}$. The latter is less soluble in hot water than in cold. The authors were not able to obtain the calcium salt mentioned by Schorlemmer crystallising with $1\frac{1}{2}\text{H}_2\text{O}$. They prepared a copper salt which, as Lieben and Rossi state, decomposes at the ordinary temperature, with formation of a basic salt. The *silver salt*, $\text{C}_5\text{H}_9\text{O}_2\text{Ag}$, crystallises in extremely minute needles. J. I. W.

Oxidation of Levulic Acid. By B. TOLLENS (*Annalen*, **206**, 257—273; this Journal, 1879, Abstr., 523).—The researches of Grote and the author (*Annalen*, **175**, 202) have shown that levulic acid probably contains five normally combined carbon atoms, and that the oxygen atom, besides those contained in the carboxyl group, is combined with its carbon atom in a ketonic combination. Conrad (*Ber.*, **11**, 2177) has established that β -acetopropionic acid is identical with levulic acid obtained from sugar, and that levulic acid has the constitution $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$. As it has been shown that the synthetic β -acetopropionic acid yields succinic acid on oxidation, the author, for the sake of comparison and to decide the constitution of levulic acid, has subjected the latter to oxidation with dilute nitric acid. Succinic, acetic, oxalic, hydrocyanic, and probably formic acid, are produced, and ammonia is found also among the products of decomposition. From these results it follows that *levulic acid has the constitution $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, and is really β -acetopropionic acid.*

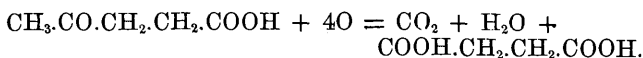
The author remarks on the formation of hydrocyanic and ammonia as products of the decomposition of carbon compounds with nitric acid, the former caused by the combination of the carbon with the nitrogen of the acid, the latter by the reduction of the acid. In these respects, the action of carbon compounds resembles the action of metals on nitric acid.

V. H. V.

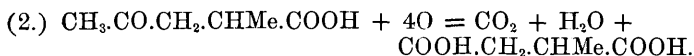
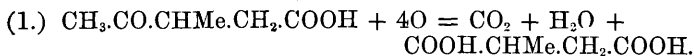
Two Homologues of Acetopropionic Acid. By C. BISCHOFF (*Annalen*, **206**, 313—337).—The author has prepared by the action of alkalis on ethylic β - and α -methylacetosuccinate the α - and β -methylacetopropionic acids, thus:—



He has also investigated whether these acids follow Popoff's law of the oxidation of ketones or undergo the same reaction as acetopropionic acid (Grote, *Annalen*, **206**, 257), which forms oxalic and succinic acids. In this reaction, the methyl radical of the acetyl group is oxidised into carbonic acid and water, while the CO attaches itself in the form of carboxyl, to the remaining nucleus of the acid thus:—



The author has shown that both the isomeric methylpropionic acids are converted into the same methylsuccinic (pyrotartaric) acid, thus:—



Ethylic β -methylacetosuccinate is prepared by the action of sodium ethylate on ethylic acetoacetate and ethylic α -bromopropionate, and distilling under reduced pressure. It boils at 238° , and on saponification with an 8 per cent. baryta solution, the barium salts of β -acetoisobutyric (α -methylacetopropionic) and of pyrotartaric acids are formed. By decomposing the former with sulphuric acid, the acid itself is obtained as a colourless oily liquid (b. p. 247 — 248°), which does not solidify even when cooled by a freezing mixture. From its method of preparation, the acid has the composition $\bar{\text{A}}\text{cCH}_2.\text{CHMe}.\text{COOH}$. By heating ethylic β -methylacetosuccinate with dilute hydrochloric acid, the same acid and its ethyl salt are formed, and may be separated by the insolubility of the latter in water. The ethyl salt, $\bar{\text{A}}\text{cCH}_2.\text{CHMe}.\text{COOEt}$, is a colourless, oily liquid (b. p. 206 — 208°), easily miscible with alcohol and ether. The salts of β -acetoisobutyric acid crystallise with difficulty, those of the alkalis and alkaline earths being syrups which show no signs of crystallisation, even when kept in a vacuum for some months. The zinc salt can, however, be obtained as a vitreous mass, but the silver salt is always contaminated by dark-coloured decomposition products. β -acetoisobutyric acid is easily oxidised by dilute nitric acid into oxalic and pyrotartaric acids.

Ethylic α -methylacetosuccinate can be prepared either by Kressner's method (*Annalen*, **192**, 137), by the action of methyl iodide on the

ethyl salt of sodium-acetosuccinic acid, or by the action of ethyl monochloracetate on the ethyl salt of methyl sodium-acetoacetate; the former method is, however, to be preferred. Kressner has already established the formation of pyrotartaric acid by the action of potash on ethyl α -methylacetosuccinate. The author has investigated the analogous action of baryta-water, and has found, besides pyrotartaric, also the ketonic β -acetobutyric acid. This latter is an oily liquid (b. p. 242°), which solidifies into a crystalline leafy mass; it is easily soluble in water, alcohol, and ether, and is very deliquescent. It has the composition $\text{Ac} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{COOH}$. The acid decomposes carbonates, and forms only soluble salts. The salts of alkalis and alkaline earths resemble those of the isomeric β -acetoisobutyric acid, in being syrups which do not crystallise.

The zinc salt forms a white warty mass, composed of thickly-grouped needles. The ethyl salt, $\text{Ac} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{COOEt}$, is a colourless oily liquid (b. p. $204\text{--}206^\circ$), miscible with alcohol and ether, but insoluble in water. β -acetobutyric acid, when oxidised with dilute nitric acid, forms oxalic and pyrotartaric acids, like the isomeric iso-acid, but the oxidation is not so easily effected. From these experiments, it follows that pyrotartaric acid is formed by the action of concentrated alkalis on the ethyl salts of α - and β -methylacetosuccinic acids, and by the oxidation of α - and β -methylacetopropionic acids.

V. H. V.

Action of Potash on Bromomethacrylic Acid. By A. R. FRIEDRICH (*Annalen*, **203**, 351—362). — Bromomethacrylic acid, $\text{CHBr} : \text{CMe} \cdot \text{COOH}$, prepared by Kekulé's method (*ibid.*, Supp. **2**, 99; also Cahours, *Ann. Chim. Phys.* [3], **67**, 129), crystallises in needles (m. p. 65° ; Cahours found 60°). When strongly heated with potash, it gives potassium bromide, potassium carbonate, allylene, methane, and acetic acid. Propaldehyde appears to be one of the secondary products produced in the preparation of bromomethacrylic acid.

T. C.

Tetrolic Acid. By A. LAGERMARK (*Bull. Soc. Chim.* [2], **35**, 171). — Silver tetrolate decomposes at the ordinary temperature, forming silver allylide. Tetrolic chloride is a somewhat unstable body, leaving a carbonaceous residue when heated above 120° . Hitherto all attempts to prepare ethyl tetrolate have failed. On passing hydrochloric acid into an alcoholic solution of tetrolic acid, ethyl monochlorocrotonate is obtained: $\text{C}_4\text{H}_4\text{O}_2 + \text{EtHO} + \text{HCl} = \text{C}_4\text{H}_4\text{ClO}_2\text{Et} + \text{H}_2\text{O}$. By treating tetrolic chloride with sodium ethylate, ethyl chloride and sodium tetrolate are produced.

L. T. O'S.

Isomerides of Lactic Acid. By H. KLIMENKO (*Bull. Soc. Chim.* [2], **34**, 321). — Liebig's extract of meat contains paralactic acid, but no ethylene-lactic acid. The properties of paralactic acid and its derivatives are similar to those of fermentation lactic acid and its derivatives, the difference being only in rotatory power; the zinc salts of both these acids may be obtained crystalline or amorphous according to circumstances. The acid obtained by adding gradually an excess

of silver oxide to a hot solution of β -iodopropionic acid and heating the mixture for some minutes, is not the hydraerylic acid of Wislicenus (which is not formed in presence of excess of silver oxide), but a crystalline acid of the formula $C_3H_4O_2$, which melts at $68-69^\circ$. It is probably a polymeride of acrylic acid, and is also formed by the action of bromine on ethylene-lactic acid in the cold.

J. 'M. H. M.

Conversion of the Hydroxyvaleric Acid from Allyldimethylcarbinol into Isopropylacetic Acid. By A. SCHIROKOFF (*J. pr. Chem.* [2], **23**, 283-288).—*Iodovaleric acid*, $CMe_2I.CH_2.COOH$ (m. p. 80°), is deposited as a crystalline mass, when a cold concentrated solution of hydroxyvaleric acid, $CMe_2(OH).CH_2.COOH$ (obtained by the oxidation of allyldimethylcarbinol), is saturated with hydriodic acid. On reduction with sodium-amalgam, iodovaleric acid is converted into isopropylacetic acid, which can be identified by the crystalline form of its silver, manganese, barium, and calcium salts.

These reactions show that the hydroxyvaleric acid from allyldimethylcarbinol is a derivative of isopropylacetic acid.

W. C. W.

Ammonium Carbonate. By E. J. MAUMENÉ (*Compt. rend.*, **90**, 926).—Two samples of commercial sesquicarbonate of ammonia were found to differ considerably in their smell and their solubility in water. One, which had a strong smell, gave a solution of density 1.14; the other, with but slight smell, gave a solution of density only 1.06. On analysis, their composition was found to be nearly identical, agreeing with the formula $(NH_3)_2(CO_2)_3(H_2O)_5$.

C. W. W.

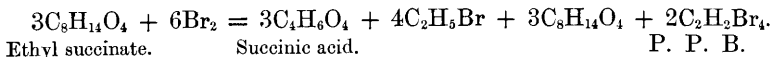
Formation of β -Methoxyglutaric Acid from Diallylmethyl Carbinol. By B. SOROKIN (*J. pr. Chem.* [2], **23**, 276-283).— β -*Methoxyglutaric acid* is formed when a solution of 5 parts of potassium permanganate in 125 parts of water is gradually added to 1 part of diallylmethyl carbinol. The precipitated manganese oxide is removed by filtration, and the filtrate acidified with sulphuric acid and extracted with ether. The ethereal solution contains two acids, which are separated by conversion into their lead salts. By decomposing the lead salt with sulphuretted hydrogen, β -methoxyglutaric acid is obtained as a syrupy liquid, which forms amorphous potassium, calcium, barium, zinc, and lead salts, all of which are easily soluble. The copper salt, $(C_6H_5O_5Cu)_2 + CuH_2O_2 + 5H_2O$, crystallises in plates, and the silver salt is also crystalline.

The insoluble lead compound previously mentioned consists of a mixture of lead oxalate and the salt of another acid, the composition of which was not ascertained.

W. C. W.

Investigation of the Product of the Action of Bromine on Ethyl Succinate. By F. URECH (*Ber.*, **14**, 340-345).—These substances were heated together in the proportion of 1 mol. of bromine to 1 mol. of ethyl succinate, in sealed tubes for 50 hours. At 100° , the mass was still coloured by free bromine. In continuing the experiment, owing to an accident the temperature rose, and the resulting mass was colourless. From it by fractional distillation several com-

pounds were separated, consisting chiefly of succinic acid, ethyl bromide, and hydrobromic acid; in smaller amounts, succinic anhydride, an acid having the composition $C_3H_4O_3$, and some brominated compounds, appear to be formed. The chief result of the action is expressed by the following equation; the $C_2H_2Br_4$ is used as a "collective formula" of purely theoretical significance:—



Decomposition of Mesoxalic Acid. By C. BÜTTINGER (*Annalen*, **203**, 138—144).—Wichelhaus having shown that pyruvic acid may be converted into mesoxalic acid, and Claisen that pyruvic acid may be obtained from acetyl cyanide, the object of this paper is to show that the relations existing between glyoxylic, pyruvic, and mesoxalic acids may be expressed by the formulæ $H.CO.CO\dot{O}H$; $CH_3.CO.CO\dot{O}H$; and $CO\dot{O}H.CO.CO\dot{O}H$.

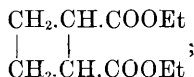
The mesoxalic acid (m. p. 108°) employed was prepared according to Drechsel's method by boiling a solution of barium alloxanate. When it is heated with water, carbonic anhydride is evolved, and at the same time a small quantity of an acid resembling glyoxylic is formed. On distilling a strong aqueous solution until the residue froths, a syrup containing glycolic and oxalic acids remains.

When sulphuretted hydrogen acts on the acid in presence of silver oxide, thioglycolic and thiodiglycolic acids are formed, and carbonic anhydride is evolved.

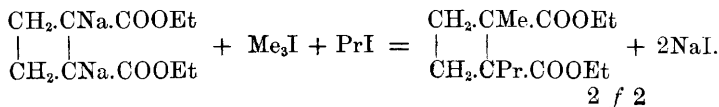
These reactions show that the molecule of mesoxalic acid is easily decomposed, yielding an oxidation product (carbonic anhydride), and a reduction product (glyoxylic acid). W. R. H.

Isobutylallylmalonic Acid. By M. BALLO (*Ber.*, **14**, 335—339).—Theoretically the ethyl salt of this acid should be obtained by the action of allyl and isobutyl iodides on ethyl disodium-malonate, $CNa_2(COOEt)_2$. The salt formed in this reaction, however, yields an acid which contains two atoms of hydrogen less than isobutylallylmalonic acid, and has the formula $C_{10}H_{14}O_4$. It is less soluble in cold than hot water, and easily soluble in alcohol and ether; it melts at 124° , and is decomposed when heated above its melting point.

The author proposes to prepare camphoric acid from ethyl disodium succinate, obtained in the same manner as the corresponding malonate, this, treated with ethylene bromide, should yield the compound



from this the disodium derivative may be prepared, which, when treated with methyl and propyl iodides, would yield ethyl camphorate, thus:—



By a preliminary experiment, a small quantity of an acid melting at 176° has been obtained; camphoric acid melts at 175 – 178° . The author is also engaged on the synthesis of adipic acid. P. P. B.

Halogen Derivatives of Fumaric and Maleic Acids. By OSSIPOFF (*Bull. Soc. Chim.* [2], **34**, 346–347).—In this preliminary note the author announces that he has obtained fumaric acid by the reduction of dibromosuccinic acid, in acid solution. When ethyl dibromosuccinate, chloromaleic acid or its ethyl salt, and bromomaleic acid are reduced in this way, the separation of the products is very difficult. J. M. H. M.

Citraconic and Mesaconic Acids. By P. KRUSEMARK (*Annalen*, **206**, 1–24).—Kekulé, Fittig, and Landolt have shown that although citraconic and mesaconic acids yield the same substance when treated with hydrobromic acid, yet with bromine they give different addition products. The author has studied some of the products of decomposition of citra- and mesa-dibromopyrotartaric acids. The former, when dissolved in sodium carbonate (in the proportion of 1 mol. acid to 2 mols. Na_2CO_3), and gradually heated, yields propaldehyde, bromomethacrylic acid, carbonic anhydride, and hydrobromic acid, the reaction taking place in precisely the same manner when a solution of the acid is heated without addition of sodium carbonate. Mesa-dibromopyrotartaric acid, when heated with sodium carbonate, yields in addition to the above products an acid isomeric with bromomethacrylic acid. *Isobromomethacrylic acid* is much more readily soluble in water than its isomeride, and crystallises in large, shining, and transparent plates (m. p. 65 – 66°). Its calcium salt is about eight times more soluble in water than the corresponding bromomethacrylate. When the aqueous solution of mesadibromopyrotartaric acid is heated without addition of sodium carbonate, it yields propaldehyde, carbonic anhydride, hydrobromic acid, and *bromocitraconic anhydride*. It is remarkable that whilst a bromo-derivative of mesaconic acid yields a derivative of citraconic acid, the corresponding bromo-derivative of citraconic acid does not under the same circumstances furnish bromocitraconic anhydride.

The author considers that the splitting up of citradibromopyrotartaric acid with formation of bromomethacrylic acid, whilst mesabromopyrotartaric acid yields besides bromomethacrylic acid an isomeric acid, confirms the formulæ given by him in a previous paper (*Annalen*, **188**, 103), namely for

Tetradibromopyrotartaric acid.
 $\text{COOH} \cdot \text{CHMe} \cdot \text{CBr}_2 \cdot \text{COOH}$

Mesadibromopyrotartaric acid.
 $\text{COOH} \cdot \text{CBrMe} \cdot \text{CHBr} \cdot \text{COOH}$

In this case bromomethacrylic acid would have the composition $\text{CHBr} : \text{CMe} \cdot \text{COOH}$, and the isoacid $\text{CH}_2 : \text{C}(\text{CH}_2\text{Br}) \cdot \text{COOH}$.

O. H.

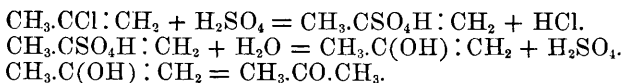
Synthesis of Glyceric Acid from Monochlorolactic Acid. By E. FRANK (*Annalen*, **206**, 338–351).—In order to decide whether glyceric acid is a carboxyl acid, or has the constitution assigned to it

by Wislicenus, the author has synthesised it thus: monochloraldehyde is converted by hydrocyanic acid into chlorethylidene hydrocyanide, and then, by dilute acids into the corresponding carboxylic compound, monochlorolactic acid, which with silver oxide should give the corresponding hydroxy acid, or glyceric acid. As it was found impossible to isolate monochloraldehyde from the crude product of the reaction of dilute sulphuric acid on monochloroacetal, hydrocyanic acid was passed into it directly, and the hydrocyanide formed converted by dilute hydrochloric acid into *monochlorolactic acid*. This acid forms micaceous prisms (m. p. 71°), easily soluble in water, alcohol, and ether, the solutions having a strongly acid reaction and taste. The calcium salt $(C_3H_4ClO_3)_2Ca + 3H_2O$, forms clinorhombic tables, sparingly soluble in cold, readily soluble in hot water.

The zinc and manganese salts also form tabular crystals with $3H_2O$; the copper salt (anhydrous) forms silky green leaflets. The methyl (b. p. $185-187^{\circ}$) and the ethyl salt (m. p. 37° , b. p. 205°) were also prepared; both are soluble in water, with salt decomposition. On comparison of the author's acid with those of Werigo and Melikoff (this Journal, 1879; Abstr., 522), and of Richter (*ibid.*, 1880; Abstr., 32), it appears that the author's is identical with the latter, but isomeric with the former. From the method of preparation, the author's acid has the composition $CH_2Cl.CH(OH).COOH$. On decomposing this acid with moist silver oxide, an acid identical in its chemical and physical properties with glyceric acid was obtained. From this method of synthesis it follows that glyceric acid is a true carboxylic acid, and has the composition $CH_2(OH).CH(OH).COOH$. V. H. V.

Action of Dehydrating Agents on Glyceric and Tartaric Acids. By E. EULENMEYER (*Ber.*, 14, 320—323).—In a former communication (*Ber.*, 13, 309), the author announced the hypothesis that all secondary alcohols containing the group $CH.OH$, united by two affinities to one carbon-atom, are in the moment of their production converted into aldehydes, and that tertiary alcohols, in which the group $C.OH$ is united by two affinities to a carbon-atom, are in like manner converted into ketones. This hypothesis has been used to explain the formation of aldehydes from glycols, and of acrolein from glycerol; also the formation of acetone from bromo- and chloro-propylene. Further confirmation of the truth of the above hypothesis is to be obtained from the study of the action of dehydrating agents on polyhydric acids, such as glyceric and tartaric acids. Both these acids, when distilled with potassium hydrogen sulphate, yield almost theoretical amounts of pyrrocemic acid. This is explained in the case of glyceric acid by the supposed formation of α -hydroxyacrylic acid, $CH_2:C(OH).COOH$, which then becomes $CH_3.CO.COOH$, in accordance with the hypothesis. In the case of tartaric acid, hydroxyfumaric acid is supposed to be formed in the first place, which, like fumaric acid, loses carbonic anhydride, and forms α -hydroxyacrylic, and finally pyrrocemic acid.

The formation of acetone from monochloropropylene by solution in sulphuric acid and distilling with water, observed by Oppenheim, is explained as follows:—



Similarly the formation of monochloracetone from dichlorglycid may be explained; this compound is also formed by distilling glycerol-monochlorhydrin with potassium hydrogen sulphate. α -Chlorostyrene, when heated with water, yields acetophenone, but β -bromostyrene yields phenylethylaldehyde.

P. P. B.

Ethyl Pyroracemate. By C. BÖTTINGER (*Ber.*, **14**, 316—317).—For the preparation of this salt, the author recommends the following method:—A mixture of equal volumes of pyroracemic acid and alcohol is mixed carefully with half the volume of strong sulphuric acid. When the mixture has cooled down, it is poured into ether floating on water. The ether dissolves out the ethyl pyroracemate, from which it is obtained on evaporation. Ethyl pyroracemate distils with decomposition at 130° ; it is a colourless, strongly refractive liquid, of ethereal odour. It is sparingly soluble in water, by which it is easily decomposed into free acid and alcohol; its aqueous solution gives a precipitate with baryta-water after a short time.

P. P. B.

Meconic Acid. By D. B. DOTT (*Pharm. J. Trans.* [3], **11**, 576).—The ordinary methods for preparing the silver meconates yield salts of very variable composition; by precipitation, compounds containing 35·02—55·81 per cent. Ag were obtained, and by boiling the bibasic salt with water, the products contained 56·45—88·87 per cent. $\text{Ag}_3\text{C}_7\text{HO}_7 = 62·18$ per cent. Ag.

The lead salts prepared by precipitation gave 56·21—64·77 per cent. $\text{PbO} : \text{Pb}_3(\text{C}_7\text{HO}_7)_2 = 65·91$ PbO per cent.

From these results, the author considers that the evidence is in favour of the dibasic nature of meconic acid.

L. T. O'S.

Double Salts of Meconic Acid. By E. H. RENNIE (*Chem. News*, **42**, 75).—Calcium chloride is first added in considerable quantity to a solution of meconic acid, and then a small quantity of ferric chloride; a red precipitate is produced, the supernatant fluid remaining colourless. If, however, the ferric salt is added in sufficient quantity, the precipitate first formed redissolves on standing, producing the well-known blood-red colour. If the solution is mixed with some ferric chloride *first*, and then the calcium salt added, no precipitate is produced at first, but (unless the iron salt be in considerable excess) a slight precipitate is deposited after a time.

The red precipitate above mentioned was prepared from recrystallised meconic acid, and gave, after thorough washing and heating to 140° , numbers representing a substance of fairly constant composition; the nearest formula appears to be $(\text{C}_7\text{H}_7\text{O})_4\text{Fe}_2\text{Ca}_3\cdot 5\text{H}_2\text{O}$. Similar compounds are produced with barium and strontium. They are slightly soluble in cold, more so in boiling water, and separate out from the latter on cooling in an amorphous condition. Their solutions give no precipitate with ammonia, and no blue coloration with potassium ferro-

cyanide, but after the addition of an acid, a brownish tint indicative of a ferrous salt. Treated with sulphuric acid and ether, an acid is produced, which strikes a blood-red colour with ferric chloride.

D. B.

Argento-antimonious Tartrate (Silver Emetic). By J. P. COOKE (*Sill. Jour.* [3], 19, 393).—This substance, formed by the action of silver nitrate on antimonious chloride dissolved in tartaric acid, is soluble in water to the extent of 1 part in 100 of boiling water, and about 1 in 500 of water at 15°; more exactly a saturated solution at 15° contains 2.76—2.68 parts in 1,000 of water.

A boiling saturated solution deposits, on cooling, the compound in colourless, brilliant, hemihedral crystals, belonging to the trimetric system.

Three analyses of the salt gave a mean of 26.30 per cent. of silver, the formula $C_4H_4Ag(SbO)_6.H_2O$ requiring 26.34 per cent. The crystals of silver emetic rapidly blacken in the light, and are easily decomposed by heat. At about 200°, they decompose with a slight explosion, free carbon being expelled, and a residue of metallic silver and antimonious oxide left.

C. W. W.

Remarks on a Note by L. Eisenberg "On the Separation of Trimethylamine from the Bodies which accompany it in Commercial Trimethylamine." By E. DUVILLIER and A. BUISNE (*Compt. rend.*, 92, 250—254).—In a note on a method of separating trimethylamine from the bodies which accompany it in commercial trimethylamine hydrochloride, by taking advantage of the feeble solubility of its platinochloride (this vol., 83), Eisenberg states that Hofmann's method of separating tertiary from primary and secondary amines by means of oxalic ether is long and inconvenient. The authors have previously so modified this process as to render it easy of execution. To the *aqueous* solution of the bases, free from ammonia, oxalic ether is added, and thus the primary amines are precipitated in the form of oxamides. The mother-liquor is mixed with potash in order to set free the bases, and the latter, after desiccation, are dissolved in absolute alcohol. Oxalic ether, which may be readily obtained by Löwig's process, is now added to the alcoholic solution, and thus the diamines, and a small quantity of monamines still remaining in solution, are converted into oxamic ethers, whilst the triamines are not affected, and may be obtained by distilling the mixture. The oxamic ethers are converted into calcium salts, and these are separated and purified by taking advantage of their unequal solubilities in alcohol and in water. This method of separation is applicable on a large scale, and when the number of bases to be separated is taken into account it is not so complicated as might at first sight appear.

Vincent first pointed out the presence of trimethylamine in the commercial product, but the authors first made known the composition of the latter, and devised a means of separating the different bases contained in it.

C. H. B.

Triacetondiamine. By W. HEINTZ (*Annalen*, **203**, 336—350).—This compound, which has the composition $\text{CO}(\text{CH}_2.\text{CMc}_2.\text{NH}_2)_3$, was prepared in quantity by a slight modification of the method previously described (*Annalen*, **201**, 106). It may also be obtained, although less readily, by the action of ammonia alone on acetone. Its *acid oxalate*, $\text{C}_9\text{H}_{20}\text{N}_2\text{O} \cdot 2\text{H}_2\text{C}_2\text{O}_4$, is much more soluble in warm than in cold water, and is insoluble in alcohol and in ether. The *neutral oxalate*, $\text{C}_9\text{H}_{20}\text{N}_2\text{O} \cdot \text{H}_2\text{C}_2\text{O}_4$, crystallises in needles, and is more soluble in water than the acid salt, but almost completely insoluble in alcohol. The hydrochloride, $\text{C}_9\text{H}_{20}\text{N}_2\text{O} \cdot 2\text{HCl}$, on long boiling in aqueous solution, is decomposed into ammonium chloride and the hydrochloride of triacetoneamine. T. C.

An Acetone Base containing Sulphur. By W. HEINTZ (*Annalen*, **203**, 236—240).—In the preparation of triacetone-diamine with the aid of carbon bisulphide, a fine crystalline body was obtained as an ethereal oxalate which appears to have the composition $\text{C}_6\text{H}_{22}\text{N}_2\text{SO}_3$.

The base decomposes very readily when in a free state.

A platinochloride was obtained with some difficulty in yellow microscopic crystals, giving on analysis $(\text{C}_3\text{H}_5\text{N}_2\text{S} \cdot \text{HCl})_2\text{PtCl}_4$, from which the free base would have the formula $\text{C}_3\text{H}_5\text{N}_2\text{S}$. The further investigation of this body was given up on account of its exceedingly unpleasant odour and the difficulty of obtaining it in quantity.

W. R. H.

Tropeïnes. By A. LADENBURG (*Compt. rend.*, **90**, 921).—Having succeeded in producing atropine by the action of hydrochloric acid on a mixture of tropine and tropic acid, the author attempted to form other alkaloïds in a similar way, substituting various organic acids for the tropic acid. He proposes to call these compounds *tropeïnes*. He has prepared and studied the tropeïnes of salicylic, metoxybenzoic, parahydroxybenzoic, amygdalic, benzoic, and phthalic acids. They are all formed more or less easily by the action of hydrochloric acid on a mixture of tropine and the acid at the heat of the water-bath.

The most important of these compounds is hydroxytoluyl (amygdalic) tropeïne, for which, on account of its being homologous with atropine, the author proposes the name *homatropine*. This compound, which is prepared in the same way as the other compounds, and may be purified by means of its hydrobromide, aurochloride or picrate, has two important advantages over atropine for ophthalmological purposes. It produces an equal dilatation of the pupil of the eye, but its effects have completely passed away at the end of 24 hours, and its poisonous action is very much slighter. C. W. W.

Oxidation of Nitroxylene and Xylidine. By WROBLEWSKY (*Bull. Soc. Chim.* [2], **34**, 332).—The author has demonstrated (1) that solid nitroxylene gives nitro-isophthalic acid by oxidation; (2) that xylidine obtained by reduction of solid nitroxylene gives, by the action of nitric acid, two nitroxylidines, one of which can be trans-

formed into the nitroxylenes, $C_6H_2MeHMe(NO_2)$, and the other into the nitroxylenes, $C_6H_3Me(NO_2)Me$. J. M. H. M.

Cuminoïn and Anisoïn. By M. BÖSLER (*Ber.*, **14**, 323—330).—These compounds, analogous to benzoïn, are obtained in a similar manner, viz., by the action of an alcoholic solution of potassium cyanide on cuminaldehyde and anisaldehyde respectively.

Cuminoïn, $C_{20}H_{24}O_2$.—The best yield of this compound was obtained by heating 10 grams of cuminol, 10 of water, 20 of alcohol, and 2 of potassium cyanide together for $1\frac{1}{2}$ hours. It crystallises in needles (m. p. 98°), and is easily soluble in alcohol, ether, and benzene, but only sparingly in water or light petroleum. Fehling's solution oxidises it in the cold, and potash or soda colours its alcoholic solution bluish-violet. It dissolves unaltered in concentrated sulphuric acid. The cuminoïn described by Raab (*Ber.*, **10**, 55) is totally distinct from this compound. Cuminoïn, reduced by the action of sodium-amalgam on its alcoholic solution, yields hydrocuminoïn (m. p. 135°), identical with that of Raab (*loc. cit.*) and Claus (*Annalen*, **137**, 92). At the same time a small quantity of a substance, melting at 186 — 194° , is formed, which is probably a pinacone.

Deoxycuminoïn, $C_3H_7.C_6H_4.CH_2.CO.C_6H_4.C_3H_7$, is obtained by reducing the alcoholic solution of cuminoïn with zinc and hydrochloric acid; it crystallises in small leaflets (m. p. 58°), is sparingly soluble in water, and easily soluble in alcohol, ether, and benzene. By heat, it is decomposed into carbon and an oil.

Cuminil, $(C_3H_7.C_6H_4.CO)_2$, is obtained by oxidising cuminoïn in a dry current of chlorine. It crystallises in yellow prisms (m. p. 84°); alcohol, ether, benzene, and chloroform dissolve it readily, whereas water and light petroleum dissolve it sparingly; it distils without decomposition.

Cuminilic acid, $(C_3H_7.C_6H_4)_2C(OH).COOH$, is obtained by heating cuminil with caustic alkalis, and is best prepared by fusion with potash. Cuminilic acid crystallises from dilute alcohol in slender colourless needles (m. p. 119 — 120°); it is sparingly soluble in water, but easily in alcohol, ether, and benzene. Sulphuric acid dissolves it, giving a yellowish-red coloration. Alkaline cuminilates are soluble, those of the alkaline earths and of the heavy metals are insoluble. Oxidised by potassium dichromate, it forms cumic acid and an oil, probably a dicumainil ketone.

Anisoïn, $C_{16}H_{16}O_4$, is obtained in a similar manner to cuminoïn from anisaldehyde; this method of preparation gives better yields than that of Rossel (*Annalen*, **151**, 33). The author confirms Rossel's description of its properties, save that the melting point is found to be 113° , and not 109 — 110° .

Anisil, $(MeO.C_6H_4.CO)_2$, is obtained by oxidising anisoïn with Fehling's solution. It crystallises from alcohol in golden-yellow needles (m. p. 133°); it is easily soluble in hot alcohol, insoluble in water, and distils without decomposition.

Anisilic acid, $(C_6H_4.MeO)_2C(OH).COOH$, is obtained from anisil by fusion with potash; it crystallises from dilute alcohol in slender colourless needles (m. p. 164°). It is sparingly soluble in water, but

easily in alcohol; its salts resemble those of cuminic acid. By heat it is decomposed, forming reddish-violet vapours. By oxidation it is converted into dimethoxybenzophenone, carbonic anhydride, and water.

Dimethoxybenzophenone, $\text{CO}(\text{C}_6\text{H}_4\text{OMe})_2$, crystallises from alcohol in beautiful colourless needles (m. p. 144°), is insoluble in water, and easily soluble in alcohol, benzene, and chloroform, and distils without decomposition. That this is the dimethoxy-derivative of benzophenone is shown by its formation when dioxybenzophenone is heated with soda and methyl iodide. Further, both these dimethoxyphenones yield the same dibromide, $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}_3$, when their solutions in chloroform are treated with bromine; the dibromide crystallises from benzene in needles (m. p. 181°), and is only sparingly soluble in alcohol, but easily in chloroform and benzene. Dioxybenzophenone has been described by Stadel and Gail, and Gräbe and Caro, Baeyer and Burkhardt (this Journal, **34**, 671, 886, and **36**, 59). Anisil, from its mode of preparation, contains the ketone and methoxyl groups in the para-position; anisilic acid and dimethoxybenzophenone are similarly constituted, as it is improbable that in the formation of anisilic acid from anisil an intermolecular change should take place. P. P. B.

Dinitro-derivatives of Deoxybenzoin. By GOLOUBEFF (*Bull. Soc. Chim.* [2], **34**, 345).—One of these is formed by the action of fuming nitric acid on deoxybenzoin. It crystallises in minute needles (m. p. 114 – 116°), soluble in 12 parts of boiling alcohol, or 565 parts of cold alcohol. Oxidised by chromic acid in acetic solution, it gives: (1) a new isomeride of dinitrobenzil (m. p. 205 – 206°), differing from the isomerides obtained by Zinin, and studied by Zagoumenny; (2) nitrobenzoic acid; and (3) nitrodracrylic acid.

The second dinitrodeoxybenzoin is formed by the action of nitric acid (1.4) on the residue from the preparation of nitrodeoxybenzoin already described by the author. It forms large yellowish needles (m. p. 125 – 126°), soluble in 24 parts of boiling and 780 parts of cold alcohol. J. M. H. M.

Compounds of Acetone and Methyl Oxide with Benzaldehyde, and the Constitution of Acetophoron. By L. CLAISEN and A. CLAPARÈDE (*Ber.*, **14**, 349–353). — *Dibenzylidene-acetone*, $\text{PhCH}:\text{CH.CO.CH}:\text{CHPh}$, is obtained by passing dry hydrochloric acid gas into a mixture of 1 mol. of acetone and 2 of benzaldehyde; the solution becomes first light red, then darker, and, on standing, crystals separate out. It crystallises from ether in colourless or pale yellow transparent quadratic tables or leaflets (m. p. 112°). It is easily soluble in chloroform, and sparingly in ether and alcohol. Sulphuric acid dissolves it, forming a deep orange liquid; with concentrated hydrochloric acid the crystals become vermillion, and are decolorised on addition of water. Baeyer (*Annalen*, Supp. **5**, 82) has studied the action of dehydrating agents on acetone and benzaldehyde, obtaining a resinous body insoluble in alcohol, and an intermediate product in the form of an oil. The authors find that after saturating a mixture of molecular quantities of benzaldehyde and

acetone, and pouring the product into water, an oil is obtained which proved to be benzaldehyde with a small quantity of dibenzylidene acetone.

Benzylidene-mesityl oxide, or *Benzylidene-isopropylidenacetone*, $\text{Me}_2\text{C} : \text{CH}.\text{CO}.\text{CH} : \text{CHPh}$. This compound is obtained in a similar manner from benzaldehyde and mesityl oxide; it is a pale yellow oil, of an agreeable odour resembling strawberries, and boils at $178-179^\circ$ under 14 mm. pressure. Its composition shows that mesityl oxide behaves differently from acetone, and it appears that condensation with aldehydes only takes place in the methyl group united with a carboxyl group. According to Claisen (*Annalen*, **180**, 4) the constitutional formula of phorone is $\text{Me}_2\text{C} : \text{CH}.\text{CO}.\text{CH} : \text{CMe}_3$, and hence it contains no methyl group united directly with a carboxyl group. Therefore phorone and benzaldehyde should not yield condensation products; this conclusion is confirmed by experiment, so that phorone may be regarded as diisopropylidenacetone. P. P. B.

Synthesis of Aromatic Aldehydes by means of Chromyl Chloride. By E. PATERNÒ and S. SCICHLONE (*Gazzetta*, **10**, 53—55).—Referring to Étard's experiments on the action of chromic dichloride, CrO_2Cl_2 , on cymene (this Journal, 1880, Abstr., 467), in which he stated that he had obtained ordinary cuminaldehyde identical with that from oil of cumin, the authors say that they have made similar experiments, and have found not only that the quantity of the oil obtained by decomposing the product of the action of chromic dichloride on cymene with water is much less than Étard gives, but that it boils at $180-230^\circ$, and not at 223° ; also that a portion only of the oil combines with sodium hydrogen sulphite, and that which is liberated from this sodium compound boils at $208-211^\circ$ when pure. This purified oil, moreover, yields toluic acid on oxidation with dilute nitric acid, and is probably a ketone.

The authors have not continued their experiments, as they were originally undertaken in the hopes of preparing propylbenzaldehyde in this manner, and they have since obtained it in another way; moreover, they did not think it right to invade another chemist's field of research, especially as they believe that the chromic dichloride reaction will give rise to important results. C. E. G.

Oxidation of Ketones. By GOLDSTEIN (*Bull. Soc. Chim.* [2], **35**, 108).—The analogy between aldehydes and ketones led to the idea that the latter might yield compound ethers by oxidation; and conversely that these might be reconverted into ketones by reduction. By this means benzophenone (m. p. $47-48^\circ$) has been obtained from phenyl benzoate. No results were obtained with ethyl acetate.

L. T. O'S.

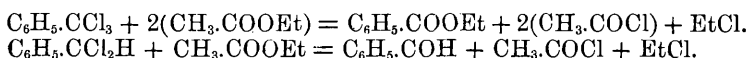
Preparation of Benzoic Acid, Benzoic Ether, and Benzaldehyde. (*Dingl. polyt. J.*, **239**, 157).—By warming 3 mols. of acetic acid with a few per cent. of zinc chloride on a water-bath, and adding 1 mol. of benzotrichloride, hydrochloric acid and acetic chloride escape, whilst the residue consists of benzoic acid and chloride of

zinc. Instead of acetic chloride, acetic anhydride may be produced by using acetate of zinc. This method, however, is not very practical, as, owing to the violence of the action, the benzoic acid is obtained in the form of benzo-acetic anhydride, which is subsequently converted into benzoic acid. Anhydrous acetate of zinc can be used with advantage, instead of chloride of zinc, at the beginning of the process.

Other organic acids can be employed instead of acetic acid, *e.g.*, formic acid; oxalic anhydride, however, acts with less power. Benzoic acid forms, under similar conditions, benzoic chloride, $\text{C}_6\text{H}_5.\text{CCl}_3 + \text{C}_6\text{H}_5.\text{COOH} = 2\text{C}_6\text{H}_5.\text{COCl} + \text{HCl}$.

By the action of benzodichloride on acetic acid and chloride of zinc, benzaldehyde, acetic chloride, and hydrochloric acid are obtained: $\text{C}_6\text{H}_5.\text{CHCl}_2 + \text{CH}_3.\text{COOH} = \text{C}_6\text{H}_5.\text{COH} + \text{CH}_3.\text{COCl} + \text{HCl}$.

Benzodi- and tri-chloride act on ethereal salts in the same manner, *e.g.*, ethyl acetate forms, besides acetic chloride and ethyl chloride, ethyl benzoate and benzaldehyde:



Ethyl alcohol with benzotrichloride gives ethyl benzoate, ethyl chloride, and hydrochloric acid. The latter is converted into ethyl chloride by using an excess of alcohol. Benzoic chloride is produced as an intermediate product. Benzodichloride behaves in a like manner with the alcohols of the fatty series. Instead of the chlorides, the corresponding benzobromides can be used; it is not advisable to employ copper or antimony chloride instead of zinc chloride. D. B.

Two Modifications of Amidocumic Acid: Acetamidocumic Acid. By M. FILETI (*Gazzetta*, 10, 12—20).—In 1874 Paternò and the author obtained two amidocumic acids by the reduction of nitrocumic acid (*ibid.*, 5, 383), one of which melted at 104° and the other at 129° , but all subsequent attempts to prepare the former failed; moreover, on examining the specimens of it which they had in their possession, the crystals were found to be opaque, and their melting point had risen to 129° . Lippmann and Lange attributed the lower melting point to the presence of an oily impurity, overlooking the fact that the acid of m. p. 104° had changed spontaneously into the one of m. p. 129° . After repeated trials, the author has succeeded in again obtaining the amidocumic acid of m. p. 104° . The nitrocumic acid* is reduced by ammonium sulphide, and, after removal of the excess of sulphide, the amidocumic acid is precipitated by acetic acid. If the pure acid is *completely* dissolved by boiling with water and then allowed to cool very slowly, on the following day, besides the acid of m. p. 129° , long very thin transparent plates (m. p. 104°) will sometimes be observed grouped around a point. It is best to operate with a small quantity of acid (0.4 gram acid and 20 c.c. water), but

* It is noteworthy that the crystals of nitrocumic acid deposited from the nitric acid solution are phosphorescent in the highest degree, emitting a bluish-white light when powdered or cut, or even when allowed to fall from the height of a few centimetres on a hard surface. The crystals formed in a benzene solution are not phosphorescent.

even with every care it is only occasionally that the plates are formed. The chances of a successful result are greater when the acid and water (5 : 10 grams) are heated in sealed tubes at 100° for an hour, and then allowed to cool very slowly. The crystals may be dried between filter-paper, but care is required, as they are readily converted into the other modification; even pressure with a hard substance will effect the change.

Acetamidocumic acid is readily obtained by the action of acetic anhydride on amidocumic acid. It is insoluble in water, and only moderately soluble in boiling alcohol, from which it crystallises in long slender needles (m. p. 248—250°). It dissolves in solutions of the alkalis or alkaline carbonates, and is decomposed into acetic and amidocumic acids when heated with water at 230°. With acetaldehyde, amidocumic acid gives a red amorphous substance which has not been examined further.

C. E. G.

Additive Compounds of Atropic Acid. By K. KRAUT and G. MERLING (*Ber.*, **14**, 330—332).—That atropic acid combines with hydrochloric acid at 137°, was first observed by Kraut (*Annalen*, **148**, 243). The authors find that this combination takes place at the ordinary temperature, but more completely at 100°, a chlorhydratropic acid being formed, which is identical with that of Spiegel (*Ber.*, **14**, 235), and yields tropic acid when treated with alkaline carbonates. When atropic acid is heated with hydrochloric acid at 140°, the chlorhydratropic acid is decomposed, and can no longer be converted into atropic acid, but yields an isomeride probably identical with Ladenburg's tropide (this Journal, **36**, 720). Moreover, atropic acid combines with hydrobromic acid at 100°, forming bromhydratropic acid, which the authors regard as different from Fittig's (*ibid.*, 379), although it has the same melting point and yields the same amido-acid when treated with ammonia. This bromhydratropic acid yields tropic acid when treated with alkaline carbonates. The authors have also observed that cinnamic acid combines with hydrochloric acid.

P. P. B.

Isatropic Acid. By R. FITTIG (*Annalen*, **206**, 34—67).—Atropic acid heated in aqueous solution for a long time, or by itself in the dry state, yields α - and β -isatropic acids, the former always in largest proportion. The products are crystallised from acetic acid diluted with an equal bulk of water, the first crystallisation, melting at 237°, being pure α -acid, the mother-liquors yielding the β -compound. The largest yield of the α -acid is obtained by heating the atropic acid in closed flasks during 24—36 hours at 140—160°, extracting the brown mass with a little strong acetic acid and alcohol, and crystallising the residue from glacial acetic acid. The pure α -acid crystallises in small globular masses of crystals (m. p. 237—237·5°), very little soluble in water even when boiling, more readily in alcohol and in glacial acetic acid.

Calcium α -isatropate, $C_{16}H_{14}O_4Ca + 2H_2O$, gradually separates from mixed solutions of the ammonium salt and calcium chloride, the separation taking place instantaneously on the liquid being heated. It is

practically insoluble in water, and only parts with its water of crystallisation when heated to 200° . The corresponding barium salt contains $2\frac{1}{2}$ mols. H_2O , and separates from its aqueous solution in crystalline crusts. *Ethyl α -isatropate* melts at $180-181^{\circ}$.

β -isatropic acid crystallises from acetic acid in two distinct forms, namely, either in well-formed, thick, quadratic, glistening tablets, remaining quite transparent when exposed to the air, and not losing weight at 130° , or in large hard aggregates of brilliant octohedral crystals containing acetic acid, $C_{18}H_{16}O_4 + C_2H_4O_2$, which they readily lose even at ordinary temperature. It crystallises from water in small, transparent, anhydrous, quadratic plates (m. p. 206°). If the β -acid is heated for some time at $220-225^{\circ}$, it turns brown, and the fused mass gradually becomes solid. It then consists entirely of the α -acid.

Calcium β -isatropate forms short thick brilliant prisms, $C_{18}H_{14}O_4Ca + 3H_2O$. The barium salt and the ethyl ether have also been prepared.

On oxidation with chromic acid in glacial acetic acid solution, both the α - and β -acids yield carbonic anhydride, anthraquinone, and orthobenzoylbenzoic acid, the latter identical with that described by Zincke and by Plaskuda (*Ber.*, 7, 987).

α -Isatropic acid, subjected to dry distillation, yields a liquid hydrocarbon, *atronol*, a well-crystallised monobasic acid, *atronic acid*, α - and β -isatropic acid, and a small quantity of an acid which does not crystallise, and which could not be obtained in a state of purity. If the distillation is conducted very slowly, the distillate consists almost entirely of atronol, if quickly, to a great extent of undecomposed isotropic acid. The distillate is rendered alkaline with sodium carbonate, the hydrocarbon removed by shaking with ether, the alkaline liquid precipitated with hydrochloric acid, dissolved in dilute ammonia, and the solution precipitated with calcium chloride. Calcium atronate separates at once; subsequently β -isatropate crystallises out.

Atronic acid, $C_{17}H_{14}O_2$, is practically insoluble in cold or hot water, readily in alcohol or glacial acetic acid, crystallising from the solution in transparent thick prisms (m. p. 164°). Its formation from isotropic acid takes place according to the equation: $C_{18}H_{16}O_4 = C_{17}H_{14}O_2 + H_2O + CO$. It is monobasic, and yields well-crystallised salts. *Calcium atronate*, $(C_{17}H_{13}O_2)_2Ca + CH_2O$, forms glistening needles, sparingly soluble in hot or cold water. The *barium salt* contains 4 mols. of H_2O , and closely resembles the calcium salt, but is somewhat more readily soluble.

Atronol, $C_{16}H_{14}$, a colourless viscous fluid of faint pleasant odour (b. p. $325-326^{\circ}$). It becomes thick at -18° , but does not crystallise. It is formed from atronic acid according to the equation $C_{17}H_{14}O_2 = C_{16}H_{14} + CO_2$. On boiling with dilute nitric acid, it yields a nitro-compound, soluble in alcohol and acetic acid, and separates from the solution as a thick yellow oily fluid.

Atronolsulphonic acid, $C_{16}H_{13}.SO_3H$, obtained by heating the hydrocarbon with concentrated sulphuric acid at about 50° (partial polymerisation taking place), crystallises from water, in which it is readily

soluble, in colourless needles, melting with partial decomposition at 130—131°. Its *barium salt*, $(C_{16}H_{13}SO_3)_2Ba$, is very little soluble in cold, much more readily in hot water, and crystallises from it on cooling in beautiful laminae of silvery lustre. The *calcium salt* contains 2 mols. H_2O , and closely resembles the barium compound. It is, however, much more readily soluble in water. Oxidised by chromic mixture it yields the same products as isatropic acid. Atronol is isomeric with Goldschmiedt and Hepf's dimethyltolane (*Ber.*, 6, 1504).

α - or β -isatropic acid heated with concentrated sulphuric acid at 40—45° dissolves, with evolution of carbonic oxide, and on diluting the solution *isatronic acid*, $C_{17}H_{14}O_2$, crystallises out. It is practically insoluble in water, readily soluble in alcohol, ether, and acetic acid. Crystallised from dilute alcohol, it forms a magma of iridescent scales (m. p. 156—157°). *Calcium isatronate* is a gelatinous precipitate, becoming heavier on boiling. It is anhydrous, and practically insoluble in water. *Barium isatronate*, $(C_{17}H_{13}O_2)_2Ba + 6H_2O$, is little soluble in cold water, and separates from its saturated boiling solution in the form of small thick prisms. Isatronic acid is *isomeric* with atronic acid, but is distinguished from it by comparison of the calcium and barium salts. Heated above its melting point, isatronic acid yields carbonic anhydride and atronol.

If sulphuric acid acts upon α - or β -isatropic acid at a temperature of 90°, the sulphonic acid of a hydrocarbon, $C_{16}H_{12}$, is formed, *atronylenesulphonic acid*, $C_{16}H_{12}SO_3$, together with a small amount of a substance insoluble in alkalis, soluble in alcohol with blue fluorescence, and crystallising in needles (m. p. 227°). Atronylenesulphonic acid is insoluble in water, but readily soluble in alcohol and acetic acid, melts with partial decomposition at 258°, and is not decomposed on heating with water or hydrochloric acid at 150°. It is readily soluble in sodium carbonate, and the solution remains perfectly clear for months *when kept in the dark*. Exposed to daylight it quickly becomes milky, instantly so in direct sunlight, and the decomposition proceeds until the whole of the acid has been decomposed. The barium salt is still more sensitive to light. The precipitate thus obtained by the action of the light is amorphous, soluble in alcohol, and crystallises from it in small colourless needles (m. p. 193°). Its composition is expressed by the formula $C_{16}H_{10}SO_2$, and is named by the author *atronsulphone*.

In conclusion, the author proposes constitutional formulæ for the various compounds described. O. H.

Atrolactic, Phenyllactic, and Atroglyceric Acids. By H. KAST (*Annalen*, 206, 24—34).—According to a previous note by the author, atrolactic and phenyllactic acids closely resemble each other in respect of their melting points and solubility. It is now shown that the two acids, as was to be expected, are entirely distinct compounds.

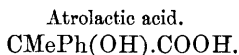
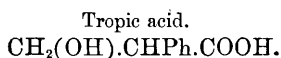
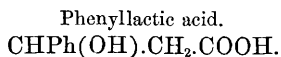
Atrolactic acid is prepared by the action of saturated hydrobromic acid on atropic acid, the resulting brominated acid being heated with sodium carbonate solution, acidified with hydrochloric acid, and the acid taken up by agitation with ether. The acid separates from its

aqueous solution in large well-formed rhombic plates, $C_9H_{10}O_3 + \frac{1}{2}H_2O$.

Phenyllactic acid crystallises without water of crystallisation.

Barium phenyllactate is little soluble in cold, more readily in hot water, separating from the solution in crystalline tufts, $(C_9H_9O_3)_2Ba + 1\frac{1}{2}H_2O$. *Zinc phenyllactate*, $(O_9H_9C_3)_2Zn + 1\frac{1}{2}H_2O$, forms a white crystalline powder, very little soluble in water.

Phenyllactic acid when boiled with baryta-water yields cinnamic acid, whilst atrolactic acid does not undergo any change under similar treatment. Hence phenyllactic acid is analogous to tropic acid in the relative position of the carboxyl and hydroxyl groups. The constitution of the three isomeric acids would be as follows:—



Atrolactic acid readily dissolves in cold hydrobromic acid, and *bromhydratropic acid*, $C_9H_9BrO_2$, soon separates from the solution in the crystalline state. Phenyllactic acid under similar conditions yields bromhydrocinnamic acid. Corresponding iodo-compounds could not be obtained.

Dibromhydratropic acid treated with alkalis or their carbonates at ordinary temperatures yields acetophenone and *atroglyceric acid*, the relative proportions of the two products depending on the quantity of alkali employed. Atroglyceric acid is very readily soluble in ether and in hot or cold water, and crystallises in small indistinct crystals (m. p. 146°). The *calcium salt*, $(C_9H_9O_4)_2Ca$, separates from water in hard crystalline nodules, the *barium* compound in glistening scales. Both salts are anhydrous. Atroglyceric acid is isomeric with the phenylglyceric or styceric acid of Anschütz and Kinnicutt, and has the constitution expressed by the formula $CH_2(OH).CPh(OH).COOH$.

O. H.

Benzidinedisulphonic Acid. By P. GRIESS (*Ber.*, 14, 300—301).—*Benzidinedisulphonic acid*, $C_{12}H_6(NH_2)_2(SO_3H)_2$, is obtained by heating benzidine with twice its weight of fuming sulphuric acid at 170° ; it crystallises in small white, usually four-sided leaflets, which are sparingly soluble in hot water, and insoluble in alcohol and ether. It is decomposed by heat, and with bromine-water gives a green coloration even in dilute solutions.

Barium benzidinedisulphonate occurs in two forms, one of which, $C_{12}H_6(NH_2)_2(SO_3)_2Ba + 5H_2O$, is obtained by slow crystallisation from water. It is soluble in hot water, and crystallises in thin shining white or six-sided leaflets. The other crystallises with $2H_2O$, and is obtained by heating the dehydrated salt with boiling water insufficient for its solution. This latter crystallises in short thick needles.

Silver benzidinedisulphonate is obtained as a white crystalline precipitate.

Tetrazo-diphenyldisulphonic acid, $C_{12}H_4N_4(SO_3H)_2$, is obtained by

treating the aqueous solution of benzidinedisulphonic acid with nitrous acid. It forms yellowish-white microscopic prisms, and is sparingly soluble in water. With naphtholsulphonic acids it forms violet- to brownish-red azo-dyes.

The formation of an isomeride of the above benzidinedisulphonic acid has been observed; it is distinguished from the above by the lesser solubility of its barium salt, and the greater solubility of its tetrazo-derivative.

In a footnote, the author states that colouring matters are obtained by the action of diazo-compounds on such bodies as phlorizin.

P. P. B.

Toluenetrisulphonic Acid. By P. CLAESSON (*Ber.*, **14**, 307—309).—Toluenetrisulphonic acid is prepared by heating 1 mol. of potassium α -toluenedisulphonate with 3 mols. of chlorosulphonic acid at a temperature gradually rising to 240° , until a portion of the mass dissolves completely in water. The product forms a hard vitreous mass on cooling. In order to prepare the trisulphonic acid from this product, it is converted into the chloride by the action of phosphorus pentachloride, and by crystallising from ether or chloroform the chloride of toluenetrisulphonic acid is obtained pure. The *chloride*, $C_7H_5(SO_2Cl)_3$, crystallises from ether or carbon bisulphide in lustrous silvery masses, and from chloroform in rhombic tables, m. p. 153° .

Toluenetrisulphonic acid, $C_7H_5(SO_3H)_3 + 6H_2O$, is obtained by decomposing the chloride with water at 130 — 140° ; it crystallises in long slender needles from water, in which it is easily soluble. At 100° , it loses 3 mols. H_2O , and the residue melts at 145° . *Potassium toluenetrisulphonate*, $C_7H_5(SO_3K)_3 + 3\frac{1}{2}H_2O$, is easily soluble in water, and at low temperatures crystallises in large rhombic tables, which weather on exposure to the air. It loses its water at 100° .

Barium toluenetrisulphonate, $(C_7H_5S_3O_9)_2Ba + 14H_2O$, is easily soluble in water, and crystallises in ill-defined forms. In a vacuum, it loses $10H_2O$; $2H_2O$ at 100° , and the remainder at 200° . *Lead toluenetrisulphonate*, $(C_7H_5S_3O_9)_2Pb + 8H_2O$, forms ill-defined crystals.

Toluenetrisulphonamide, $C_7H_5(SO_2NH_2)_3$, is insoluble in water, soluble in warm ammonia, and crystallises in microscopic crystals, which melt with decomposition above 300° .

P. P. B.

Sulphamine- and Hydroxy-acids derived from Mesitylene.

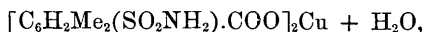
By O. JACOBSEN (*Annalen*, **206**, 167—206).—*Orthosulphaminemesitylenic Acid*.—Hall and Remsen obtained an acid which they considered to be the para-compound; the author finds, however, that it is the ortho-acid which is so formed. He prepares it by boiling for two days a mixture of mesitylenesulphonamide, potassium dichromate, sulphuric acid, and water. On cooling, the sulphaminemesitylenic acid separates out, together with some unattacked mesitylenesulphonamide. By extracting with sodium carbonate, saturating the solution cooled to 0° with carbonic anhydride, repeatedly shaking with ether, and precipitating the acid from the solution of the sodium salt with hydrochloric acid, it may be obtained pure. It melts at 263° (corr.). It is almost insoluble in cold, and only slightly

soluble in hot water, easily in alcohol and ether. On heating with lime, the acid gives metaxyol, (m. p. 176—177°). The *barium salt*, $[\text{C}_6\text{H}_2\text{Me}_2(\text{SO}_2\text{NH}_2).\text{COO}]_2\text{Ba} + 3\text{H}_2\text{O}$, crystallises in silky hemispherical masses, which lose their water of crystallisation at 100°. The *calcium salt*, $[\text{C}_6\text{H}_2\text{Me}_2(\text{SO}_2\text{NH}_2).\text{COO}]_2\text{Ca} + 5\text{H}_2\text{O}$, is very soluble in water. It crystallises in vitreous prisms. The *copper salt*, $[\text{C}_6\text{H}_2\text{Me}_2(\text{SO}_2\text{NH}_2).\text{COO}]_2\text{Cu} + 3\text{H}_2\text{O}$, is obtained by precipitating a hot dilute solution of the barium salt with copper sulphate. The filtrate yields light blue needles on evaporation. The anhydrous salt is dark green. The *sodium salt* is very soluble; it crystallises from a very concentrated solution in silky needles.

If the chromic mixture be allowed to act on the mesitylenesulphonamide for several days, until on cooling no unattacked substance separates out, sulphamineuvitic acid is formed.

On fusing with potash, orthosulphaminemesitylenic acid yields mesitylenic acid; and mesitylenic acid is also formed with soda, but the action takes place at a very high temperature, and is accompanied by a secondary reaction; carbonic anhydride is evolved, and metaxyolsulphonamide is formed. The author therefore concludes that the acid is an ortho-compound.

Parasulphaminemesitylenic acid is formed in small quantities along with the above acid by the action of chromic acid on mesitylenesulphonamide. It is best prepared by heating a mixture of mesitylenesulphonamide with potash, potassium permanganate, and water for 12 hours, and may be separated from the ortho-acid by neutralising the dilute boiling ammoniacal solution with hydrochloric acid. The ortho-compound is precipitated immediately, and the para-acid separates out during the cooling. The pure acid melts at 276° (corr.). By heating with concentrated hydrochloric acid at 200°, it gives mesitylenic acid, like the ortho-compound. The author finds that mesitylenic acid obtained in this way melts at 169—170°. The *barium salt* of the para-acid, $[\text{C}_6\text{H}_2\text{Me}_2(\text{SO}_2\text{NH}_2).\text{COO}]_2\text{Ba} + 2\text{H}_2\text{O}$, crystallises in stellate groups of long silky needles. It is much more soluble than the corresponding ortho-salt. The *calcium salt*, $[\text{C}_6\text{H}_2\text{Me}_2(\text{SO}_2\text{NH}_2).\text{COO}]_2\text{Ca} + 2\text{H}_2\text{O}$, crystallises in vitreous prisms, and is less soluble than the ortho-salt. The *copper salt*,



crystallises from a warm dilute solution in ultramarine-blue monoclinic prisms. It is decomposed by potash. The *sodium salt* only crystallises from very concentrated solutions.

Sulphamineuvitic Acid.—The author prepares this acid by further oxidising sulphaminemesitylenic acid by means of potassium permanganate. He finds that the acid obtained from the ortho-acid is identical with that prepared from the para-compound. The product, therefore, must be considered to be orthoparasulphamineuvitic acid.

Anhydrosulphamineuvitic acid, $\text{C}_9\text{H}_7\text{O}_5\text{NS}$, is obtained by decomposing the acid potassium salt. It dissolves in 20 parts of boiling water, but is not easily soluble in cold water. It is extremely soluble in alcohol and ether. It melts at 270—272° (corr.).

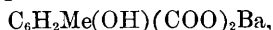
The Salts of Sulphamineuvitic Acid.—The normal barium salt, $C_9H_7O_6NSBa$, is obtained by heating the anhydro-acid with barium carbonate. The potassium salt, $C_9H_7O_6NSK_2$, is very soluble in water; by heating the hot dilute solution with hydrochloric acid, the acid potassium salt, $C_9H_5O_6NSK$, is formed. The normal ammonium salt is obtained by neutralising the acid with ammonia.

Sulphouvitic Acid.—The acid potassium salt,

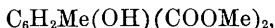


is easily soluble in hot water. It crystallises in large rhombic plates. The free acid is obtained by suspending the lead salt in water and decomposing it with sulphuretted hydrogen; it crystallises in small pointed crystals, which are anhydrous, best in the presence of a small quantity of sulphuric acid. The normal barium salt, $(C_6H_5SO_3)_2Ba$, is obtained by heating the free acid with barium carbonate. It crystallises in short needles containing no water of crystallisation. The author finds that by boiling with soda or hydrochloric acid, sulphamineuvitic acid loses ammonia.

Hydroxyuvitic Acid.—The author considered it probable that the hydroxyuvitic acid formerly obtained by him from α -hydroxymesitylenic acid and from mesitol (*Annalen*, 195, 287) was the diortho-compound. He finds, however, that with superheated hydrochloric acid, it gives ortho- and not para-cresol, so that it would seem probable it is the ortho-para-acid. He has prepared a hydroxyuvitic acid from sulphamineuvitic acid, and finds that it is not identical with that obtained from mesitol. The free acid is very soluble in alcohol, but almost insoluble in chloroform. It is obtained in very large crystals of $\frac{1}{4}$ — $\frac{1}{2}$ cm. diameter, when a stream of hydrochloric acid gas is passed into a warm dilute alcoholic solution, and the liquid is allowed to cool. It melts at about 290° with partial decomposition. It sublimes when heated between watch-glasses. The normal barium salt,



separates out from a tolerably concentrated solution in warty gelatinous masses. The normal calcium salt, $C_6H_2Me(OH)(COO)_2Ca + 2H_2O$, is precipitated when the acid is boiled with calcium carbonate and a small quantity of milk of lime. The acid calcium salt, $[C_6H_2Me(OH)(COO_2)]_2H_2Ca + 2H_2O$, is obtained by heating the acid with an insufficient quantity of calcium carbonate. The basic calcium salt is formed by the action of milk of lime on the normal salt. The dimethyl salt of orthoparahydroxyuvitic acid,



is obtained by passing hydrochloric acid gas into a methyl alcohol solution of the acid, and then distilling with steam. It crystallises from dilute alcohol in large pointed needles (m. p. 128°). (The dimethyl salt of the diortho-acid melts at 79° .) The liquid which remains when the dimethyl salt has been separated gradually deposits needles of *hydroxy-ethyluvitic acid*, $C_6H_2Me(OH)(COOEt)COOH + H_2O$. It is completely saponified by boiling with concentrated soda solution. The calcium salt, $[C_6H_2Me(OH)(COOEt).COO]_2Ca$, crystallises from an aqueous solution in nodules composed of fine needles.

The author shows that the hydroxyuvitic acid obtained from orthohydroxymesitylenic acid is the diortho-acid, and that obtained from sulphamineuvitic acid is the ortho-para-acid. He states that his diortho-acid is probably identical with Böttinger's β -hydroxyuvitic acid (*Annalen*, **189**, 181), but thinks it unlikely that Böttinger's α -acid is the ortho-para-compound.

Sulphaminetrimetic Acid.—The acid potassium salt is obtained from the bye-products formed in the oxidation of sulphaminemesitylenic acid. It is very soluble in water.

Hydroxytrimetic acid is obtained by fusing the potassium salt of sulphaminetrimetic acid with potash. When pure, it crystallises from an aqueous solution in very long silky needles. The author proves this acid to be identical with that obtained by Ost (*J. pr. Chem.*, **14**, 110).

Azo-derivatives of Toluene. By J. BORSIŁOWSKY (*Annalen*, **207**, 102).—Paratoluidine sulphate on oxidation in alkaline solution with potassic ferricyanide yields about 60 per cent. of two products, a red and a yellow body, both of which are somewhat insoluble in cold alcohol, the red one almost entirely so. The yellow substance (m. p. 144°) is identical with the parazotoluene obtained by Petrieff from nitrotoluene (*Ber.*, **3**, 549). The red substance crystallises from ether or benzene in fine rhombohedral crystals, containing forms R. —2R. and ∞ P2. Analysis gives the empirical formula as C_7H_7N . It melts at 244° , and decomposes a little above that temperature. It does not give salts with acids, and is with difficulty reduced by ammonium sulphide to a hydrazo-compound. The hydro-compound forms white brilliant tabular crystals (m. p. 171 — 172°). The results of analysis point to the formula $C_{14}H_{16}N_2$ or $C_{28}H_{36}N_4$. On nitration a nitro-body was obtained giving figures on analysis $C_{14}H_{11}(NO_2)_3N_2O$ or $C_{28}H_{20}(NO_2)_6N_4O$.

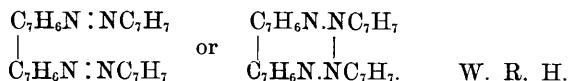
From the formation of an acetyl derivative, and also from salts of the hydrazo-compound it is possible that the red body has the formula $C_{14}H_{14}N_2$, a parazotoluene (?).

Metazotoluene.—The preparation of this body was attempted both by oxidation of metatoluidine and by reduction of metanitrotoluene. The body obtained by reduction with sodium amalgam forms red rhombic crystals (m. p. 54 — 55°) of the form P, ∞ P ∞ , ∞ P ∞ . It easily forms supersaturated solutions in alcohol. The hydrazo-compound formed by the action of ammonium sulphide is a colourless oil.

Metatoluidine on oxidation with potassic ferricyanide gives a yellowish body of m. p. 219° , which is not metazotoluene.

The oxidation of orthotoluidine did not yield any product which could be isolated or purified. The same also applies to methylaniline, naphthylamine, and toluylenediamine.

The author is finally of opinion that the red body from paratoluidine has one of the two formulæ—



Isomeric Xylidines. By E. WROBLEWSKY (*Annalen*, **207**, 91—101).—Of the three possible isomeric xylidines derived from meta-xylene, $\text{Me} : \text{Me} : \text{NH}_2 = [1 : 3 : 4]$, $[1 : 3 : 5]$, and $[1 : 3 : 2]$, the two last have been investigated by the author.

Isoxylene (b. p. $140\text{--}141^\circ$) was purified and nitrated; and the nitroxylene (b. p. $235\text{--}245^\circ$) reduced to xylidine, and converted into the acetyl derivative, when it was observed that another xylidine was formed, probably derived from orthoxylene, which has been shown by Jacobsen (*Annalen*, **144**, 275) to be present in coal-tar xylenes.

On nitration the acetoxylidine (m. p. 127°) gives acetonitroxylidine, $\text{CH}_2\text{Me}_2(\text{NO}_2)\cdot\text{NH}\cdot\text{Ac}$, separating from its alcoholic solution in white crystals (m. p. 180°).

On treatment with strong sulphuric acid it yields nitroxylidine, $\text{C}_6\text{H}_2\text{Me}_2\text{NO}_2\cdot\text{NH}_2$, in red crystals, volatile in steam (m. p. 76°); these by Griess' reaction are converted into a nitroxylene, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NO}_2$, yellow needles, (m. p. 67° ; b. p. 255°).

On reduction, this nitroxylene yields a xylidine, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2$, as a colourless liquid (b. p. $220\text{--}221^\circ$) not solidifying at -20° , which gives beautiful crystalline salts with acids. Its aceto derivative forms large flat needles (m. p. $144\cdot5^\circ$).

The above-mentioned xylidine is probably symmetrical, substitution in aromatic amines being generally quite regular. The analogy is further supported by the bromination-products of xylidine.

The author has also obtained the third isomeric nitroxylene from the nitroxylidine.

Separation of Orthoxylene from its Isomerides, and preparation of the Xylidine.—Jacobsen (*Ber.*, **10**, 1010) first noticed the presence of orthoxylene in coal-tar xylene, and separated it by means of its sulphonic derivative. This separation is better effected by conversion of the mixed xylenes into the xylidines, ortho- and meta-, and heating for three days with glacial acetic acid. The whole being then fractionally distilled, yields a fraction up to 310° , consisting of water, acetic acid, and unchanged xylidine acetate, metacetxylide coming over above 320° .

The fraction under 310° , on treatment with a potash solution, separates an unchanged xylidine, which may be distilled with steam, and again heated with glacial acetic acid. On distillation, the fraction under 310° contains the greater part of the unchanged (ortho) xylidine, the fraction above 320° consisting of a mixture of the acetyl derivative of this with metaxylidine. The new xylidine, $\text{Me} : \text{Me} : \text{NH}_2 = [1 : 2 : 4]$, is a colourless liquid (b. p. 215°), of sp. gr. 9942 at 20° , not solidifying at -20° . It gives crystalline salts with acid.

The corresponding acetxylide forms white tables (m. p. $131\text{--}132^\circ$), sparingly soluble in water.

An attempt to obtain the hydrocarbon by the action of nitrous acid on this xylidine in alkaline solution failed to give any definite result, a body being formed similar in properties to the one obtained by Jacobsen (*Ber.*, **10**, 1009) by the direct nitration of orthoxylene.

The table exhibits the differences and properties of the three xylidines arising from their structure.

	[1 : 3 : 4].	[1 : 2 : 4].	[1 : 4 : 5].
Xylidine, b. p.	212°	215°	220—221°
M. p. of aceto-derivative..	127°	131—132°	138—139°
Hydrochloride	anhydrous	+ $\frac{1}{2}$ OH ₂	+ OH ₂ .
			W. R. H.

Action of Ammonia on Isatin. By E. v. SOMMARUGA (*Wien. Akad. Ber.*, [2], 82, 307—318).—The author in two former papers in the same publication (July, 1876, and May, 1877), described three derivatives of isatin obtained by acting on it with alcoholic ammonia, under pressure; and he regarded these bodies as substitution products of isatin, on the supposition that its formula was C₁₆H₁₀N₂O₄.

Shadwell and Claissen's experiments (this Journal, 1879; Abstr., 534) pointed to the formula C₈H₅NO₃, and this was supported by Baeyer (Abstr., 1879, 937). In the present paper the author defends his own view. Isatin contains at least one hydroxyl group which can be exchanged for an amido-group by the action of ammonia, and it is only on this supposition that the formation of C₁₆H₁₁N₃O₃ from C₁₆H₁₂N₂O₄, by the action of dilute potash, can be explained. But if isatin contains a hydroxyl group, Baeyer's formula does not express its constitution. The author thinks it proved that monamidoisatin contains two of the oxygen atoms as a quinone group (O₂), and dihydromonamidoisatin two hydroxyl groups in their place.

G. T. A.

Tetraphenylethane. By ZAGOU MENNY (*Bull. Soc. Chim.* [2], 34, 329—330).—The author has prepared tetraphenylethane by the action of nascent hydrogen (tin and hydrochloric acid) on diphenylcarbinol, or its ether, dissolved in acetic acid. The reaction with the latter substance is $\text{CHPh}_2\text{O.CHPh}_2 + \text{H}_2 = \text{CHPh}_2\text{CHPh}_2 + \text{H}_2\text{O}$. The symmetrical formula given above for tetraphenylethane differs from the unsymmetrical one given by Thörner and Zincke, based on the transformation of β -benzopinacolin, $\text{CPh}_3\text{CO.Ph}$, into tetraphenylethane by the action of hydriodic acid. The author has repeated these

experiments, but assigns to β -benzopinacolin the formula of $\begin{array}{c} \text{Ph}_2\text{C} \\ | \\ \text{Ph}_2\text{C} \end{array} \text{O}$, observing that it has not the characters of a ketone. It is not reduced by tin and hydrochloric acid, nor by zinc and acetic acid; boiling potassium hydrate gives triphenylmethane and benzoic acid (?).

J. M. H. M.

Diphenylparaxylylmethane and Diphenylnaphthylmethane. By HEMILIAN (*Bull. Soc. Chim.* [2], 34, 326).—*Diphenylparaxylylmethane*, produced by the action of phosphoric anhydride or sulphuric acid on a solution of benzhydrol in paraxylene, forms large tabular crystals, melting at 91°. *Diphenylnaphthylmethane*, obtained by treating in the same way a mixture of benzhydrol and naphthalene, crystallises in shining needles, melting at 150°.

J. M. H. M.

Diphenylenephenylmethane and Diphenylenetolylmethane. By HEMILIAN (*Bull. Soc. Chim.* [2], 34, 325—326).—These hydrocarbons, identical with those obtained by the action of phosphoric

anhydride on solutions of fluorenic alcohol in benzene or toluene, are easily produced by the action of aluminium chloride on the chloride corresponding with fluorenic alcohol, dissolved in excess of benzene or toluene. J. M. H. M.

Diphenylbenzenes. By SCHMIDT and SCHULTZ (*Annalen*, **203**, 118—137).—The authors have repeated the original experiment of Berthelot, of passing benzene-vapour through a tube, at a bright red heat, and have obtained a number of hydrocarbons, in addition to diphenyl.

From the fractions boiling above 260° the following bodies have been isolated :—

Diphenylbenzene, $C_{18}H_{14}$, crystallises from hot alcohol in fine shining plates (m. p. 205° ; b. p. 283° ; under 45 mm. it boils at 250°). It gives a dinitro-product, sparingly soluble in alcohol, and crystallising in long monoclinic needles (m. p. 277°).

On oxidation, it appears to give a nitrodiphenylenecarboxylic acid (m. p. 290°), not identical with the acid of m. p. 252° , obtained directly from paradiphenylenecarboxylic acid.

Trinitrodiphenylbenzene, $C_{18}H_{11}(NO_2)_3$, forms slender rhombic crystals (m. p. 195°). It is not oxidised by chromic acid. On reduction it appears, however, to give an amido-body, melting at 169.5° .

Isodiphenylbenzene, $C_{18}H_{14}$, is easily separated from diphenylbenzene by the difference in their solubility in alcohol. It crystallises in long needles (m. p. 85° ; b. p. 363°).

The yield of isodiphenylbenzene from benzene is about 2 per cent. It gives a trinitro-product (m. p. 200°), which also resists oxidation by chromic acid. On oxidation, a basic substance, melting at 288° , is obtained.

Isodiphenylbenzene, when oxidised with chromic acid, yields benzoic acid, paradiphenylcarboxylic acid, and another acid in very small quantity, of the composition of a diphenylcarboxylic acid, and giving a soluble barium salt.

Benzerythrene, $C_{24}H_{18}$. This substance is left as an insoluble powder on treating the dark coloured very high boiling products with alcohol.

Its best solvent is benzene, from which it crystallises in colourless plates (m. p. 307° and 308°) which become strongly electrical when warmed.

Triphenylene, $C_{18}H_{12}$. This body was separated from the alcoholic washings of the crude benzerythrene as a picric acid compound. It is probably identical with Berthelot's triphenylene, and isomeric with chrysene and the body of the formula $C_{18}H_{12}$, obtained by one of the authors by the action of sodium on bromobenzene.

A number of oily products of very high boiling points, and not forming compounds with picric acid, were also formed, but have not been investigated. W. R. H.

Oxidation of α - and β -Dinitronaphthalene by Nitric Acid. By BEILSTEIN and KOURBATOFF (*Bull. Soc. Chim.* [2], **34**, 327).—The specific gravity of the nitric acid employed was 1.15° , and the temperature 150° . α -Dinitronaphthalene furnishes ordinary nitrophthalic

acid, dinitrobenzoic acid, and picric acid. β -Dinitronaphthalene gives dinitrophthalic acid, melting at 266° , dinitrobenzoic acid, and picric acid. The barium salt of the diuinitrophthalic acid produced in the latter case is a crystalline powder, insoluble in water. The hydrogen ethyl salt, $\text{COOH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COOEt}$, crystallises in needles, fusible at 186° . Ethyl dinitrobenzoate melts at 91° . J. M. H. M.

Methylnaphthalene. By F. REINGRUBER (*Annalen*, **206**, 367—380).—By fractional distillation of those portions of coal-tar oil which boil between 220 — 270° , the author has separated an oil, intermediate in its boiling point between naphthalene and acenaphthene. This hydrocarbon was purified by exposing the various fractions to the cold of winter, and separating out the oil from the other hydrocarbons, which solidify at a temperature of -12° to -20° . By treatment with soda, and then with fuming nitric acid, the hydrocarbon was obtained, mixed with water and other impurities. These latter can only be removed by distillation over phosphoric anhydride, and treatment with chromic acid mixture: purified in this way, the hydrocarbon has the composition of methylnaphthalene, $\text{C}_{11}\text{H}_{10}$. It is a colourless, faintly blue, fluorescent oil, which solidifies at -18° to -20° into a solid mass of crystalline structure, melting above -18° . It is miscible in all proportions with alcohol, ether, benzene, &c., insoluble in water, but passes over in a current of steam. This methylnaphthalene is isomeric with the methylnaphthalene obtained by Fittig (*Annalen*, **155**, 112) from α -bromonaphthalene and methyl iodide.

Synthetical methylnaphthalene.

Sp. gr. at $11.5 = 1.10287$

B. p. 231 — 232°

At -18° fluid.

From coal-tar.

Sp. gr. at $22^{\circ} = 1.0042$

B. p. 243°

At -18° solid.

The hydrocarbon from coal-tar is then probably β -methylnaphthalene. The author isolated the barium salt of β -methylnaphthalenesulphonic acid ($\text{C}_{11}\text{H}_9\text{SO}_3$) $_2\text{Ba}$, as a white salt, showing no signs of crystallisation. The preparation of oxidised compounds and nitro-derivatives failed; a bromo-compound was obtained, but only in an impure state. The author has found naphthalene even in portions of coal-tar boiling at 253° ; above that temperature diphenyl was found. V. H. V.

Nitroso- β -naphtholsulphonic Acid. By R. MELDOLA (*Chem. News*, **42**, 175).—By mixing a solution of a salt of β -naphtholsulphonic acid (mono) with a solution of sodium nitrite in equivalent quantities, and acidulating with dilute hydrochloric acid, a deep orange-coloured liquid is obtained from which the barium salt of nitroso- β -naphtholsulphonic acid is precipitated on adding ammonia and barium chloride. This acid appears to form two classes of salts, typified by the barium compounds $\text{C}_{10}\text{H}_5(\text{NO})(\text{HO})\cdot\text{SO}_3 > \text{Ba}$, and $\text{C}_{10}\text{H}_5(\text{NO}) < \text{O} > \text{SO}_3 > \text{Ba}$.

The former crystallises in large flat orange needles with 1 mol. H_2O ,

and the latter in microscopic green needles with 2 mols. H_2O . The most characteristic reaction of the nitroso-sulphonic acid is that with the phenols and amines, which results in the formation of a series of red and violet colouring matters. D. B.

Commercial Lemon Oil. By F. FLAVITZKY (*Bull. Soc. Chim.* [2], 35, 171—172).—Commercial lemon oil of rotatory power $[\alpha]_D = +60^\circ$ contains, besides the right-handed terebenthene, a left-handed one (b. p. 165°), having the properties of French terebenthene; its sp. gr. is 0.857 at 20° , and $[\alpha]_D = -29.8^\circ$; it forms a hydrochloride having the rotatory power $[\alpha]_D = -25.9^\circ$. From the large quantity the oil contains (above 10 per cent.), it would appear to be an adulteration. If the dextrorotatory terebenthene (b. p. 177° , sp. gr. 0.8443 $[\alpha]_D = +92.3$) were perfectly pure, its rotatory power would in all probability be higher and nearer to that of orange oil, which is above $+100^\circ$. With hydrochloric acid gas in presence of moisture it readily yields a dihydrochloride, and also when hydrochloric acid is passed into its ethereal or acetic acid solution. L. T. O'S.

The Terebthenes. By F. FLAVITZKY (*Bull. Soc. Chim.* [2], 34, 342—343).—The author considers liquid terebenthene hydrochloride to be a mixture of the solid hydrochloride and the dihydrochloride. The dihydrochloride is formed, according to Berthelot, by the action of hydrochloric acid on terebenthene solutions, whilst the solid hydrochloride is produced by the action of hydrochloric acid on terebenthene itself. The author finds that the formation of the one or the other depends on the solvent, terebenthene in carbon bisulphide giving the hydrochloride, whilst terebenthene in aqueous or alcoholic solution furnishes the dihydrochloride. The hydrochloride is formed directly from the terebenthene, whilst the formation of dihydrochloride is probably preceded by hydration, and is accompanied by isomerisation.

The author has succeeded in retransforming terpene dihydrochloride into terpene, by placing it in contact with dilute alcohol; in fact, the formation of terpene dihydrochloride depends on the strength of the hydrochloric acid used, a dilute solution causing the inverse change. The author has also studied the hydration of lævorotatory terebenthene from French turpentine by a solution of sulphuric acid in alcohol. 1 part terebenthene ($\alpha_1 = -33^\circ$) placed in contact with $1\frac{1}{2}$ parts alcohol (90 per cent.) and $\frac{1}{2}$ part sulphuric acid (1.64) for 12 hours, dissolves to the extent of three-fourths, and water precipitates from the solution a substance with rotatory power $\alpha_1 = -40^\circ$. This substance is not homogeneous, only half of it dissolving in sulphuric acid and alcohol; by fractional distillation in a current of steam a substance, $\text{C}_{10}\text{H}_{18}\text{O}$, is obtained with rotatory power $\alpha_1 = -56.2^\circ$. This the author calls lævorotatory hydrate of terebenthene. It dissolves in alcoholic sulphuric acid, losing its rotatory power; on adding water, it yields terpene; hydrochloric acid gas transforms it into inactive dihydrochloride; treated with acetic anhydride, it yields a new lævorotatory (iso) terebenthene ($\alpha_1 = -61^\circ$) boiling above 175° , and a substance whose composition approaches that of an acetic salt of lævorotatory terebenthene hydrate. The lævorotatory

isoterebenthene is transformed into dihydrochloride by hydrochloric acid. The author thinks it should be classed with lævorotatory terebenthene from oil of elemi, which has an equal and opposite rotatory power to the terebenthene from citron oil. In dissolving terebenthene in a mixture of sulphuric acid and alcohol, some portion is converted into terebenthenesulphuric acid, which, when treated with water, yields a hydrate and a hydrocarbon. J. M. H. M.

A New Property of Camphor. By M. BALLO (*Ber.*, **14**, 334—335).—When an excess of camphor is brought into a hot alcoholic solution of camphor containing from 36—65 per cent., the camphor forms a liquid compound floating on the top of the solution (m. p. 66—71°). This liquid after solidifying and drying at the ordinary temperature contains but traces of alcohol. P. P. B.

Liquid Camphor. By W. ALEXEJEFF (*Bull. Soc. Chim.* [2] **35**, 107).—In continuing the researches of F. Wreden (this Journal, **36**, 69) on liquid camphor, the author finds that its analysis does not agree with the formula for camphor, but on fractionation a liquid (b. p. 175—179°) is obtained whose composition is very close to that of cymene, and their densities are identical (0.814).

By the action of fuming hydrochloric acid on liquid camphor at 170° for 20 hours, a liquid is obtained separating into two fractions, one (b. p. 180—190°) probably containing cymene, and the other, boiling above 200°, containing solid camphor. L. T. O'S.

Oxidation-products of Camphor. By M. BALLO (*Ber.*, **14**, 332—333).—The author replies to Kachler (this Journal, **38**, 559) who states that the adipic acid observed by the author amongst the oxidation-products of camphor (*ibid.*, 50), is identical with hydro-oxycamphoronic acid. The reasons adduced by Kachler for regarding hydro-oxycamphoronic acid as bibasic are regarded as insufficient, as the results of the analysis of its acid, calcium and ammonium salts, may be equally well explained by viewing them as mixtures of acid and neutral calcium adipate, and of ammonium adipate and adipic acid respectively. P. P. B.

Action of Bromine and Chlorine on Nitrocamphor. By R. SCHIFF (*Gazzetta*, **10**, 21—27).—As the action of nascent hydrogen or alcoholic potash on bromonitrocamphor gives rise to the formation of a phenol (nitrocamphor) by the substitution of an atom of hydrogen for one of bromine, it seemed probable that the group, OBr, existed in bromonitrocamphor. To confirm this, it was necessary to replace the hydrogen of the OH group in nitrocamphor by bromine; accordingly a cold aqueous solution of potassium nitrocamphor was treated with bromine in the right proportion, when a substance crystallising from alcohol in splendid needles was obtained closely resembling bromonitrocamphor in appearance, but melting at 94—95° instead of 104°. On analysis its formula was found to be $C_{30}H_{43}N_3Br_2O_{14}$, and it may be regarded as derived from bromonitrocamphor and nitrocamphor as follows: $2C_{10}H_{14}(OBr).NO_2 + C_{10}H_{14}(OH).NO_2 + 5O =$

$C_{30}H_{43}N_3Br_2O_{14}$. When this substance in toluene solution is boiled with sodium corresponding to 4 atoms, sodium nitrocamphor is precipitated, whilst bromonitrocamphor remains in solution. Alcoholic potash acts energetically on it, potassium bromide is formed, and nitrocamphor is found in the solution, exactly as in the case of bromonitrocamphor.

When chlorine is passed into a solution of potassium nitrocamphor, a white pulverulent precipitate is obtained which may be crystallised from dilute alcohol. The chlorinated product thus obtained has an odour of turpentine, melts at 110° , and is insoluble in acids and alkalis. The analyses gave results corresponding with the formula $C_{30}H_{43}N_3Cl_2O_{11} = 2C_{10}H_{14}(OCl).NO_2 + C_{10}H_{14}(OH).NO_2 + 2O$. The compound, therefore, contains 3 atoms of oxygen less than the bromine derivative previously described.

The author is engaged in experiments to ascertain in what way these oxygen atoms are united with the bromonitrocamphor and nitrocamphor in the new substance.

C. E. G.

Decomposition of Glucosides by Heat. By H. SCHIFF (*Ber.*, 14, 302—304).—*Aesculin* (m. p. $204.2-205^\circ$) heated at 230° is decomposed into aesculetin and glucosan, thus:



Phlorizin melts at 110° (Stas 109°) to a semi-fluid opaque mass; by further heat it becomes solid, and melts again at $170-171^\circ$ ($158-163^\circ$ Stas); when heated to temperatures slightly below 170° , the product consists of glucosan and phloretin. J. Loewe (*Zeits. Anal. Chem.*, 15, 28) finds that phlorizin is decomposed at 130° into phloretin and glucose, $C_6H_{12}O_6$; the formation of the latter the author regards as due to its regeneration from glucose. Phloretin melts at 253° and 255° to a brownish-red mass.

Arbutin melts at $166-167^\circ$; it is undecomposed at 200° .

Salicin melts at 201° ; by continued heat at $230-240^\circ$ it is partially decomposed into saliretin and glucosan.

Helicin melts at 174° , and yields but little salicaldehyde even when heated at $185-194^\circ$, being resolved into a gummy mass.

P. P. B.

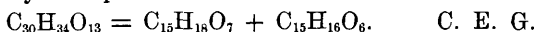
A Modification of Helicin. By H. SCHIFF (*Ber.*, 14, 317—319). If helicin, moistened with dilute nitric acid and dried by exposure to the air, is heated at $110-115^\circ$, a portion is converted into an amorphous modification insoluble in the solvents of crystalline helicin; it is without action on the yellow solution of rosaniline in sulphurous acid; it does not melt, and decomposes when heated to $220-250^\circ$. Amorphous helicin is only resolved into glucose and salicaldehyde after continued boiling with dilute sulphuric acid, whereas the crystalline variety is easily decomposed. The amorphous may be converted into the crystalline variety by crystallising it from warm dilute hydrochloric acid. Crystalline helicin is converted into the amorphous variety by heating it at $180-185^\circ$. The author regards the

amorphous helicin as a polymeride of anhydrous helicin, the crystalline variety having the formula $3C_{13}H_{16}O_7 + 2H_2O$. P. P. B.

Glucoside from the Ivy. By L. VERNET (*Compt. rend.*, **92**, 360—362).—Ivy leaves, collected in December, bruised, and exhausted with water, were treated with alcohol, and the alcoholic extract evaporated to dryness. The residue was extracted with benzene, and the insoluble matter then boiled with acetone, which deposited the glucoside on cooling. This glucoside crystallises in mammillary groups of silky colourless needles, which have a slightly sweet taste and a neutral reaction. At 22° , its freshly-prepared alcoholic solution has a lævorotatory power for $[\alpha]_D = -47.5^\circ$. It dissolves easily in alkalis in the cold, is insoluble in water, chloroform, and petroleum, is slightly soluble in acetone, benzene, and ether when cold, but dissolves in these liquids when hot. Its best solvent is boiling alcohol at 90° . At 233° it melts, becoming slightly coloured; at higher temperatures it is decomposed, and burns without residue. The glucoside has no action on Fehling's solution, but when boiled with dilute sulphuric acid, it yields a sugar and a neutral body. The sugar crystallises on the slow evaporation of its alcoholic solution in bulky transparent crystals, which have a decided sweet taste, reduce Fehling's solution, and are not fermented by yeast. The rotatory power of its solution in cold water, immediately after preparation, for $[\alpha]_D = +98.58^\circ$; the day after it was only $[\alpha]_D = +76.2^\circ$. The neutral body forms fine prismatic needles without taste or smell, melting between 278° and 280° . With solvents it behaves like the original glucoside, but is less soluble in alcohol, and does not dissolve in alkalis. Its dextrorotatory power for $[\alpha]_D = +42.6^\circ$. Its composition is $C_{26}H_{44}O_6$, that of the glucoside being $C_{32}H_{54}O_{11}$. According to this formula, the glucoside should give 29.2 per cent. of its weight of sugar; the author obtained 28.3 per cent. The ivy leaves do not contain more than 0.4 to 0.5 per cent. of glucose. C. H. B.

Remarks on the Chemical Nature of Picrotoxin. By E. PATERNÒ and A. OGLIALORO (*Gazzetta*, **10**, 36—52).—The authors, after a brief summary of the earlier researches on picrotoxin, criticise the recent paper by Barth and Kretschy (this volume, p. 286). Of the three compounds stated by them to be present in *Cocculus indicus*, "annimirtin" has never been in the authors' hand, as the material they employed was obtained from Kahlbaum, and had already been purified by several crystallisations. They consider the "picrotoxin" and "picrotin" of Barth and Kretschy to be products of decomposition of the true picrotoxin formed during the repeated boiling with benzene, "picrotin" being identical with the hydrate of picrotoxide, $C_{15}H_{18}O_7$ (this Journal, 1879, Abstr., 729); whilst the "picrotoxin" is a new compound, for which the authors propose the name of *picrotoxinin*, to distinguish it from the true picrotoxin contained in *C. indicus*. The authors moreover adhere to the formulæ originally given by them, and show that the results of Barth and Kretschy's analysis are in accordance with them.

The decomposition of picrotoxin into picrotin, $C_{15}H_{15}O_7$, and picrotoxinin, $C_{15}H_{15}O_6$, may be expressed thus:—



Waldivin. By C. TANRET (*Bull. Soc. Chim.* [2], **35**, 104—105).—The powdered fruit of *Simaba waldivia* is exhausted with alcohol, the solution distilled, and the residue, whilst warm, treated with chloroform. The chloroform solution is evaporated to dryness, and the residue exhausted with water. On cooling, the aqueous solution deposits *waldivin*, $C_{18}H_{24}O_{10} \cdot 5H_2O$, in hexagonal prisms, terminating in double pyramids. It may be purified by recrystallisation and treatment with animal charcoal. On heating, the crystals first lose their water of crystallisation, and then melt at 230° , slightly changing in colour. Waldivine is optically inactive, soluble in chloroform and in alcohol of 70° , sparingly in water, but more so in presence of acids and salts; insoluble in ether. It is neutral, has an intensely bitter taste, and is precipitated by tannin and ammoniacal lead acetate. It is dissolved, apparently without change, by sulphuric and nitric acids. Caustic alkalis and alkaline carbonates decompose waldivin, giving a yellow solution, which reduces Fehling's solution, and turns the plane of polarisation to the right. The yellow colour is destroyed on addition of an acid. The alkaline solution has no bitter taste.

L. T. O'S.

Acid from Viscum Album. By PAVLEVSKY (*Bull. Soc. Chim.* [2], **34**, 348).—The leaves of *Viscum album*, boiled with water acidified with nitric acid, yield an acid crystallising in large clinorhombic prisms, slightly soluble in water, insoluble in alcohol and ether, having the empirical formula $(CH_3O_3)HO$, and melting at 101 — 103° . The silver salt is explosive.

J. M. H. M.

Cape Tea. By H. G. GREENISH (*Pharm. J. Trans.* [3], **11**, 569—572).—This name is given to a drug (also called "Honig-thee") used at the Cape of Good Hope as a substitute for tea. It consists of the stalks and leaves of *Cyclopia longifolia* and other species of the same genus (order Leguminosæ). The microscopical examination is given (*ibid.* [3], **11**, 549).

Chemical examination.—By treating a concentrated aqueous decoction of the stalk and leaves with neutral lead acetate, a dark-brown precipitate is obtained; a further precipitate of a lighter colour is obtained by treating the filtrate with basic lead acetate, and the filtrate from this precipitate yields a bright-yellow precipitate with potash. The first precipitate was freed from lead by suspension in water and treatment with sulphuretted hydrogen, the solution evaporated to dryness, and the residue exhausted with alcohol. From the alcoholic solution, a pale reddish substance was deposited. On mixing the mother-liquor with ether, a further quantity of the red compound was obtained. This compound gave a rose-red coloration when boiled with hydrochloric acid; it is very hygroscopic. The analyses of the two preparations gave results corresponding with the formulæ $C_{25}H_{28}O_{13}$ and $C_{25}H_{28}O_{13} \cdot 2H_2O$.

For the investigation of this body, a larger quantity of it was pre-

pared by digesting an aqueous decoction with lead hydrate, suspending the precipitate in alcohol (50 per cent.), decomposing it as above, concentrating the solution under reduced pressure, and evaporating in a vacuum to a syrupy consistency. The residue was treated with absolute alcohol, and the solution filtered from insoluble matter. The filtrate (200 c.c.) was fractionally precipitated with ether (200, 300, and 400 c.c.), when the red compound, *cyclopin*, separated; the last fraction being the purest, was analysed, and gave results corresponding with the formula $C_{22}H_{26}O_{13}H_2O$. The differences in the composition may be attributed to the hygroscopic nature of the substance when boiled with dilute acids. Cyclopin assumes a bright-red colour, and, on standing, the solution deposits red flakes of *cyclopia-red*, $C_{15}H_{22}O_{10}$; grape sugar is also formed; it is therefore a glucoside. Cyclopin is insoluble in benzene, ether, light petroleum, chloroform, and carbon bisulphide, but very soluble in water. It dissolves in concentrated sulphuric acid, with a red-brown colour. With Fröhde's reagent it gives a violet-red coloration, and with potash a brown-red solution is obtained, with green fluorescence. It gives precipitates with copper, lead, and silver solutions; in neutral solutions, ferric chloride gives an olive-green colour; in presence of hydrochloric acid a yellowish, and of ammonia a brown. Potassium dichromate and hydrochloric acid give a brownish-red colour. Cyclopia-red is sparingly soluble in water, ether, light petroleum, chloroform, and benzene, but when freshly precipitated, it is readily soluble in alcohol. With alkalis it gives wine-red solutions, and with ferric chloride a brown colour. In presence of ammonia, it gives violet precipitates with calcium chloride and alum.

Cyclopin does not yield quinone when distilled with manganese dioxide and sulphuric acid, nor do the other isolated substances. Stenhouse, however (*Annalen*, **27**, 257), obtained that body from a decoction of the leaves of *Cyclopia latifolia*, prepared with milk of lime. Cyclopin, however, seems to be analogous to the tannic acids of the cinchona barks, in that it splits up into sugar and a red compound on treatment with dilute acids, but it differs from them by not precipitating gelatin and tartar emetic solutions. On concentrating the ether-alcohol filtrate obtained in the preparation of cyclopin, it yielded a crop of sulphur yellow acicular crystals of cyclopiafluorescin, $C_{14}H_{16}O_2$, insoluble in carbon bisulphide, alcohol, and ether, soluble in water and in alkalis, with a yellow colour and green fluorescence. With sulphuric acid and Fröhde's reagent, it gives yellow colours; concentrated nitric acid gives a yellow colour changing to black, and finally brown. Ferric chloride gives a green colour, changing to brown on heating; excess of nitric acid, added to the aqueous solution, gives a dark-red colour, changing to yellow; copper acetate, a grey precipitate; and potassium dichromate and hydrochloric acid, a dark brown-red. The filtrate from the lead hydrate, when treated with absolute alcohol, yielded a yellow precipitate, readily soluble in water; the aqueous solution gave a brown coloration with ferric chloride, and a precipitate with barium nitrate soluble in nitric acid. The alcoholic filtrate gave a yellow precipitate with baryta-water. These bodies are probably organic acids not precipitated by lead.

The residue obtained, after treating the syrupy extract with alcohol in the preparation of cyclopin, is a pale-red powder, readily soluble in water, sparingly in alcohol, and of the formula $C_{25}H_{30}O_{16}$, which, written $C_{25}H_{25}O_{15} \cdot H_2O$, shows it to be *oxycyclopin*. Like cyclopin, it is a glucoside, and yields *oxycyclopia-red*, $C_{19}H_{22}O_{12}$, and grape-sugar when boiled with dilute acids. In their reactions these bodies resemble cyclopin and cyclopia-red.

The residue of the leaves, after maceration with water, yielded to absolute alcohol, chlorophyll, a soft resin, a fat, and a substance probably belonging to the class of phlobaphenes. The residue gives a dark-brown-infusion with potash.

A quantitative analysis of the leaves shows the following comparison with tea from *Thea*:—

	Tea from <i>Thea</i> .	Tea from Cyclopin.
Moisture.....	8·0—12·0	20·4
Ash.....	4·5—5·5	3·7
Substances soluble in water.....	30·0—33·0	30·4
Total nitrogen	4·15—6·72	2·29
Mucilaginous substances	5·3—6·4	?

Metarabin (?).—After treating the leaves twice for 36 hours with separate quantities of soda solution (0·5 per cent.), and precipitating the two infusions, 6·51 per cent., metarabin (?) was obtained. The very small quantities of nitrogen contained in the Cape tea show that it has little or no nourishing properties. Owing to the small quantity of substance at the author's disposal, many of the above results require confirmation.

L. T. O'S.

Cape Tea. By A. H. CHURCH (*Pharm. J. Trans.* [3], 11, 693).—The author points out that *Cyclopia fluorescin* (see preceding abstract) had previously been discovered by himself under the name of *cyclopic acid*, in *Cyclopia Vogelii*, a plant used by the Boers as a substitute for tea (*Chem. News*, 22, 2). He assigns to it either the formula $C_7H_8O_4$ or $C_{14}H_{16}O_8$, the latter agreeing more closely with the results of analysis. The acid yields highly fluorescent solutions with alkalis.

L. T. O'S.

Pyridine Bases. By O. DE CONINCK (*Compt. rend.*, 92, 413—416). The author (this vol., 56) has shown that the action of potash on cinchonine gives rise to lutidine, collidine, and parvoline. The crude quinoline, when submitted to fractional distillation, yields a small quantity of methylamine, and a base of the formula of lutidine, passing over between 150° and 160°. It would seem therefore that two lutidines are obtained by the action of potash on cinchonine.

By the slow oxidation of lutidine, b. p. 165° (*vide supra*) with dilute potassium permanganate, a crystalline acid is obtained (m. p. 230—231°) very soluble in hot water and in alcohol. It sublimes at 150°. From the analyses of the acid and its salts, it would seem to be

identical with nicotinic acid, $C_6H_5NO_2$ (m. p. 229—230°). The copper salt, $C_6H_4NO_2 \cdot CuOH$, is basic and amorphous.

Lutidine of the formula, $C_5H_3NMe_2$, should on oxidation yield a bibasic acid; it however yields the acid $C_5H_4N \cdot COOH$.

If the methyl groups are in the ortho-position, then one would be easily destroyed by oxidation. Lutidine, however, may be ethyl pyridine, $C_6H_4N \cdot C_2H_5$, when on oxidation the ethyl-group would yield carboxyl; Wichnegradsky confirms this conclusion, but Weidel obtained from the oxidation of Dippel oil two isomeric acids of the formula $C_5H_3N(COOH)_2$.

Besides the bases, neutral substances were obtained, and isolated by shaking the strongly acid solution with ether, and fractionating the extract. Four fractions were obtained; that passing over at 115—130° contained amyl acetate (b. p. 124—125°). The other fractions which have an ethereal odour, have not been investigated.

L. T. O'S.

Reduction of Quinoline. By A. CLAUS and P. HIMMELMANN (*Ber.*, **14**, 339—340).—In this communication, the authors reply to König, who claims priority for the reduction of quinoline by zinc-dust and acetic acid. By the reduction of an aqueous alcoholic solution of quinoline with sodium amalgam in the cold, a product is obtained, differing from that obtained when the reaction takes place in warm solution (*Ber.*, **13**, 2048).

P. P. B.

Reduction of Quinoline and Ethylpyridine. By WICHNEGRADSKY (*Bull. Soc. Chim.* [2], **34**, 339—340).—Pure quinoline (b. p. 233°) when treated with tin and hydrochloric acid, is converted into a liquid boiling constantly at 244°, and having the composition of *tetrahydroquinoline*, $C_8H_{11}N$. This substance is a secondary amine, and gives with ethyl iodide an oily product (b. p. 255°) having the composition $C_8H_{10}Et_2N$, and this when again treated with ethyl iodide, is transformed into an iodide undecomposable by alkalis, but giving by the action of silver oxide and water a hydrate, $C_8H_{10}EtN \cdot HO$, having strong alkaline properties. Tetrahydroquinoline easily furnishes substitution products by the action of benzoic chloride, acetic anhydride, &c. The acetyl derivative is liquid, and boils at 295°, the benzoyl derivative crystallises from alcohol in large colourless tables. Tetrahydroquinoline reduces gold trichloride, ferric chloride, &c.; chromic acid reconverts it into quinoline.

Ethylpyridine, produced by the decomposition of cinchonine, gives on reduction by sodium and alcohol, a product of peculiar odour, difficult of separation from the ethylpyridine. By fractional distillation, acting on it with ethyl iodide, decomposing the crystalline product by an alkali and again distilling, a volatile alkali was obtained, boiling at 175°, and having the composition of *ethylated hexhydroethylpyridine*, C_8H_9EtN . This base combines with ethyl iodide, producing a compound ammonium iodide undecomposable by alkalis, decomposable by silver hydrate. Thus both quinoline and ethylpyridine (and probably other members of these series) furnish secondary amines by fixation of hydrogen.

The author concludes: 1st, that the pyridic and quinolic groupings

easily give rise to complex combinations, like most of the alkaloids; 2nd, that the decomposition of most alkaloids does not furnish hydroquinolic and hydropyridic bases because of the tendency of these bodies to become oxidised; and 3rd, that the fixation of 4 atoms of hydrogen by quinoline is at the expense of the two double linkings in the pyridic part of the molecule, since ethylpyridine fixes 6 hydrogen atoms.

J. M. H. M.

Cotarnine. By E. v. GERICHTEN (*Ber.*, **14**, 310—316).—The hydrochloride of cotarnamic acid described by Matthiesen and Foster as $C_{11}H_{13}NO_4.HCl$, the author finds when dried at $110-120^\circ$, loses 1 mol. H_2O , and the analysis of the dried substance shows it to be $C_{11}H_{11}NO_3.HCl$. On exposing a solution of this hydrochloride to the air, it becomes green, and a similarly coloured solution with red fluorescence is obtained by treating the hydrochloride with sodium nitrite; both exhibit the general characters of the chlorophyll absorption spectrum.

The author confirms the observations of Wright on the formation of tarconine, $C_{11}H_9NO_3$, and bromotarconine, $C_{11}H_8BrNO_3$, by the action of heat on the bromine addition-products and bromine substitution-products of cotarnine; also of the production of a blue insoluble compound obtained by heating bromotarconine at $235-238^\circ$, to which Wright attributes the formula $C_{20}H_{14}N_2O_6$.

Nartine, $C_{20}H_{16}N_2O_6$, the hydrochloride of this base, is obtained by heating bromotarconine in sealed tubes with hydrochloric acid at $120-130^\circ$; carbonic anhydride, methyl chloride, and bromide are also formed. The hydrochloride crystallised from concentrated hydrochloric acid has the formula $C_{20}H_{16}N_2O_6.2HCl$. Its aqueous solution when warmed gives a flocculent precipitate of needle-shaped crystals, containing the basic salt $C_{20}H_{16}N_2O_6.HCl$, and the neutral salt. The basic salt is sparingly soluble in water, and loses hydrochloric acid when boiled with water. The free base can be obtained from the solution of the hydrochloride by treating it with sodium bicarbonate or acetate, as an orange-red precipitate; it becomes dark red, and finally brown when dried over sulphuric acid. The solutions of the hydrochloride give with platinum chloride a yellow precipitate, becoming dark green; with copper acetate a brown gelatinous precipitate, soluble in mineral acids; with barium and calcium acetate white precipitates which become brown. Ferric chloride gives a deep brown coloration, and silver nitrate is reduced. The hydrochloride when heated becomes green, finally black, and melts at 275° to a bluish-black mass, which dissolves in water, forming a bluish-green solution. The free base is decomposed by heat. A concentrated solution of the hydrochloride when decomposed by soda is coloured first reddish-brown, becomes darker, and finally deposits a bluish-green precipitate, which is soluble in water. The alkaline solutions are decolorised by exposure to the air. The base when oxidised by potassium permanganate yields pyridinecarboxylic acid, m. p. above 250° . Heated with lime, or zinc-dust, the base yielded pyridine. Concentrated sulphuric acid dissolves the base, forming a yellow solution, which becomes red on warming.

When bromotarconine is heated with water in sealed tubes at 150—160°, it is decomposed, and yields the hydrobromides of two bases, which may be separated by the difference of solubility in water, viz.:

(1.) *Cupronine hydrobromide*, $C_{21}H_{18}N_2O_6HBr$, is sparingly soluble in water; in hot water it dissolves with a deep blue colour, which changes to a violet; the base is precipitated from these solutions by sodium bicarbonate. Sodium carbonate and caustic soda dissolve the base; it is also soluble in concentrated sulphuric acid, forming a red liquid.

(2.) *Tarnine hydrobromide* is soluble in water, the base is precipitated from the solutions by carbonate of soda or caustic soda.

Tarnine, $C_{10}H_9NO_3$, crystallises in long, slender, orange-red, lustrous needles, which lose water in a vacuum over sulphuric acid, and become scarlet; it is soluble in hot water and alcohol, insoluble in ether. Its solution in concentrated sulphuric acid is colourless, but becomes brownish-red on warming.

P. P. B.

Distillation of Cinchonine with Zinc. By M. FILETI (*Gazzetta*, 10, 20—21).—The mixture of zinc and cinchonine was distilled in glass retorts immersed in a bath of iron filings, which the author strongly recommends for similar operations, and also for ordinary use instead of a sand-bath. The distillate contained quinoline, lepidine, and a base boiling at about 30° in a vacuum, besides other bases boiling at higher temperatures, and not yet isolated. On treating the residue in the retort with hydrochloric acid, a zinc compound crystallising in very slender needles was obtained.

C. E. G.

The Mydriatic or Pupil Dilating Alkaloids. By A. LADENBURG (*Annalen*, 206, 274—307).—In this paper the author gives an account of his investigation on the relation of the alkaloids extracted from the plants of the Solanum family, which are characterised by their physiological action on the oculomotor and sympathetic nerves.

The bases described are atropine, $C_{17}H_{23}NO_3$; hyoscyamine, $C_{17}H_{23}NO_3$; and hyoscine, $C_{17}H_{23}NO_3$, from *Hyoscyamus niger*. Nearly the whole of the paper has been already published in the *Berichte* at various times, and has been abstracted in this Journal.

Hyoscine, $C_{17}H_{23}NO_3$.—Former researches have shown that in the hyoscyamus there is probably present another alkaloid besides hyoscyamine. By precipitating the crude product obtained from the mother-liquor of the hyoscyamine with gold chloride, the author has obtained the aurochloride of the new alkaloid. This salt forms slightly glistening crystals (m. p. 196—198°), less soluble in dilute hydrochloric acid than hyoscyamine aurochloride. The platinochloride forms small octohedral crystals, the picrate prismatic crystals. This alkaloid the author names "Hyoscine." From analyses of the gold and picric acid salts it is found to be an isomeride of atropine and hyoscyamine, $C_{17}H_{23}NO_3$.

Attempts at the preparation of the alkaloid in the crystalline state failed. Hyoscine, when heated with baryta-water, forms an acid identical in properties with tropaic acid. After separation of the

latter with ether, a base was obtained distilling at 241° (tropine 229°). From this difference of its boiling point, the crystal measurements of the platinochloride, and the readiness with which the base deliquesces, it follows that this base is not identical, but is isomeric with tropine, $C_8H_{15}NO$.

The aurochloride forms rhombic crystals (m. p. 198°), the picrate and mercuriochloride were also prepared. The qualitative reaction as well as the physiological action of hyoscyamine and hyoscyne are similar; further researches on the therapeutic action of the latter are promised.

V. H. V.

Citrate of Caffeine. By J. U. LLOYD (*Pharm. J. Trans.* [3], **11**, 760).—To effect combination between caffeine and citric acid, they must be treated with a solvent which exerts nearly the same action on both bodies. For this purpose, 1 part caffeine is dissolved in 14.5 parts chloroform and 1 part citric acid in 7.25 parts alcohol; the solutions are mixed and evaporated over a water-bath to a syrupy consistency. On cooling and stirring, the mass crystallises. It consists chiefly of citrate of caffeine, but contains some free base and acid; it is a semi-crystalline granular powder, permanent in the air and soluble in a mixture of alcohol and chloroform (1 to 2). It is decomposed by cold water and alcohol (sp. gr. $0.835-0.805$), and is insoluble in carbon bisulphide and chloroform. The microscopical examination shows that the substance contains two classes of crystals, but no analyses are given. The author, however, concludes that the body is a definite compound decomposed by solvents which dissolve citric acid readily and caffeine sparingly.

L. T. O'S.

Pilocarpine. By PÖHL (*Bull. Soc. Chim.* [2], **34**, 340—341).—The author has confirmed the formula $C_{23}H_{34}N_4O_4$, given by Kingzett for this alkaloid, by analysis of the alkaloid itself and its hydrochloride and platinochloride. To procure the pure alkaloid, the leaves of *Pilocarpus officinalis* are digested in 1 per cent. hydrochloric acid, the solution treated with lead acetate and filtered, the alkaloid precipitated from the filtrate by phosphomolybdic acid, and the precipitate washed with dilute hydrochloric acid and decomposed by baryta at a temperature below 100° . Pilocarpine, by dry distillation, yields a product having the chemical and optical properties of conicine. The molecular rotatory power of pilocarpine dihydrochloride depends upon the relative quantity of inactive matter.

J. M. H. M.

Bark of Alstonia Spectabilis. By O. HESSE (*Annalen*, **203**, 170—173).—The author has made an examination of the alkaloids contained in the bark of *Alstonia spectabilis*, which is closely related to *Echites scholaris*, and finds it to be richer in the dita bark alkaloids than the bark of *Echites scholaris* itself.

From 50 grams of the bark the author obtained 0.066 gram ditamine, 0.423 gram echitammonium oxide, and a residue weighing 0.042 gram, consisting of an amorphous and a crystalline alkaloid, the latter of which he supposes to be Scharlée's alstonamine.

As these barks contain six times more echitammonium oxide than

the dita barks, the use of them as a medicine in cases of intermittent fever, for which it is used in Batavia and Java, would seem to be somewhat dangerous, as it resembles curarine in its physiological action.
W. R. H.

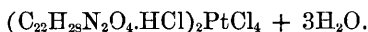
Alkaloids from Dita Bark. By O. HESSE (*Annalen*, 203, 144).—The author finds that the dita bark contains three alkaloids—ditamine, echitamine, and echitenine.

Ditamine exists in the bark to the extent of 0·04 per cent. It differs from the alkaloids associated with it in being precipitated from acid solutions by ammonia. It is easily soluble in dilute acids. A further difference is that the concentrated acetic acid solution of ditamine, remains clear on the addition of a few drops of strong hydrochloric acid, whilst echitamine gives a white crystalline precipitate. A platinochloride of the composition $(C_{16}H_{19}NO_2.HCl)_2.PtCl_4$, was obtained from ditamine, the alkaloid would therefore be $C_{16}H_{19}NO_2$.

Echitamine.—On evaporating the neutralised liquid from which the ditamine had been extracted, and adding hydrochloric acid and sodium chloride, impure echitamine hydrochloride is precipitated as a crystallisable resin; or stick potash may be added to the alkaline liquid left, after removing ditamine and the echitamine extracted by shaking with chloroform.

The purified base crystallises in thick vitreous prisms. When air-dried it has the composition $C_{22}H_{28}N_2O_4 + 4H_2O$; but when dried in a vacuum it loses $3H_2O$, and the remainder at 105° . On treating it with acids, the original base is formed. The removal of the water by drying at 105° renders its basic characters less marked. The author calls the base containing one molecule of water, echitamine hydrate or echitammonium hydroxide. It melts at 206° , and is laevorotatory. With strong sulphuric acid, an intense purple-red is produced, which fades on warming; with strong nitric acid, it gives a purple-red, becoming intense green after a few minutes.

Echitammonium hydrate is probably the strongest alkaloid known; it neutralises acids perfectly and yields well crystallised salts, many of which are described. The platinochloride has the formula—



Oxyechitamine (?).—An aqueous solution of echitammonium hydrate becomes brown on evaporation in the air, and undergoes oxidation, a substance being formed of the composition $C_{22}H_{28}N_2O_5$. It is slightly basic, sparingly soluble in water, easily soluble in alcohol and in chloroform. It has a bitter taste. The hydrochloride and yellow platinochloride are amorphous.

Echitenine is prepared from the mother-liquors of echitammonium chloride, by precipitating with mercuric chloride, decomposing the precipitate with sulphuretted hydrogen, and then shaking with chloroform. The base has the formula $C_{20}H_{27}NO_4$. It is of a brownish colour, strongly bitter, and melts above 120° . It dissolves with red violet colour in strong sulphuric acid, and in nitric acid with purple colour, becoming green and ultimately yellow. With vapour of nitric acid it

gives an intense blue-green. The salts are amorphous. The platino-chloride, dried at 100° , has the composition $(C_{20}H_{24}NO_4.HCl)_2 + PtCl_4$ and exists in the bark to the extent of only 0.01 per cent.

The author believes these alkaloids to belong to one and the same series.

Ditamine	$C_{16}H_{19}NO_2$
?	$C_{18}H_{23}NO_3$
Echitenine	$C_{20}H_{27}NO_4$
Echitammonium hydroxide..	$C_{22}H_{30}N_2O_5$

The latter is the most decidedly basic substance that *Alstonia scholaris* is capable of producing. W. R. H.

Albuminoids in Milk. By DANSLEWSKI and P. BADENHAUSEN (*Bied. Centr.*, 1880, 820).—The result of the researches on the above substance is as follows: casein is a mixture of two substances, consisting of albumin, which is probably identical with serum albumin and of protalbin, a transition-product formed during the peptonisation of various albumins with alkalis and pancreatin (this Journal, 1878, 989). It is this latter which imparts to casein its acid character. In the milk globules is an albumin which constitutes the serum of the same. In the whey are three albumins; the chief albumin present is identical with the stroma-albumin of the milk globules; an albumin of albuminoid character, named by the authors orroproteïn, belonging to the class of syntoprotalbins. After these two substances are precipitated, peptones still remain dissolved in the filtrate.

E. W. P.

Mycoproteïn. By F. SCHAFER (*J. pr. Chem.* [2], 23, 302—304).—Mycoproteïn, previously described by the author and Nencki (*J. pr. Chem.* 20, 443—465, and this Journal, 1880, Abstr., 176), on fusion with potash, yields phenol, leucine, fatty acids, and traces of indole and skatole. Mycoproteïn is completely precipitated from its solution by the addition of 2 per cent. of sodium chloride. W. C. W.

Legumin. By A. BLEUNARD (*Compt. rend.*, 90, 1080).—When legumin is heated with barium hydrate, ammonia, carbonic, oxalic, and acetic acids are produced, together with a residue containing tyrosine, alanine, valeric leucine, and various glucoproteïns, the reaction being sensibly the same as that of barium hydrate on albumin. C. W. W.

Preparation of Peptones. By A. CATILLON (*Pharm. J. Trans.* [3], 11, 759—760).

Meat Peptone.—Two parts of lean beef are treated with 12.5 parts dilute hydrochloric acid (1 in 320) and a slight excess of pepsine, which can only be determined by experiment. The mixture is agitated from time to time, and the temperature maintained between 40° and 50° . At the end of six hours, the mixture becomes fluid and almost transparent, when it contains a mixture of peptones and syntonin, coagulable by heat or nitric acid. After 12 hours, the solution is filtered (the filtrate should not be coagulated on heating or addition

of nitric acid), neutralised with sodium carbonate, and evaporated until a pellicle forms on the surface. The solution, sp. gr. 1.15, then contains one half of its weight of peptones, and is of a dark yellow colour, has a slight smell and acid taste. If the operation is not successful, the resulting solution, of a brown colour, soon becomes turbid and acquires a strong smell and unpleasant taste.

Fibrin peptone may be prepared in a similar manner.

Egg peptone is similarly prepared, the albumin being previously coagulated to promote the conversion.

Milk Peptone.—The preparation of milk peptone cannot be readily accomplished, owing to the slight action of pepsine on milk fats.

L. T. O'S.

Physiological Chemistry.

Duration and Composition of the Increase in Live Weight of Lambs when Fattening. By E. KERN and H. WATTENBERG (*Bied. Centr.*, 1880, 805—819).—The final results of the investigation instituted to determine whether young animals put on flesh more rapidly when fed with a normal allowance of food from the first, or when fed with special fattening foods under cover, and which of these methods insures that the best use of the food be made, were as follows: It is most economical for the production of good meat, that sheep of about 18 months old be fattened as rapidly as possible, with the more concentrated foods. Valuable analyses of the various parts of the slaughtered animal, as regards fat, meat, &c., are given, as well as more detailed analyses of these parts as regards albumin and ash.

E. W. P.

Fluid Meat. By S. DARBY (*Zeitschr. f. Biol.*, **16**, 208—211).—This paper is a reply by Darby to the remarks made on fluid meat by Rubner (*Zeitschr. f. Biol.*, **15**, 485; this Journal, 1880, Abstr., 904). The analyses of fluid meat made by Rubner differ so widely from those made by the author and others, that he thinks some comment is called for. Rubner came to the conclusion that fluid meat contained only 30 per cent. peptone. The author quotes the analyses of Stenhouse and Groves against this statement. They found that 11·8 per cent. of the substance (dried at 100° C.) was soluble in boiling alcohol, and that after evaporation of the solution only traces of peptone were found in the residue. The total nitrogen of the material (dried at 100° C.) estimated by Dumas' method was found to be 11·68 per cent. Another portion (dried at 100° C.) was precipitated by Schmidt's method with sodium phosphotungstate, care being taken to keep the mixture acid with phosphoric acid, and treated in the same manner, dry fluid meat yielding 102·5 per cent. dry peptone precipitate (peptone and phosphotungstate compound), which gave, by Dumas' method, 8·419 per cent. nitrogen; hence 72·09 per cent. of the nitrogen contained in fluid

meat is contained in that part of it which is precipitable by sodium phosphotungstate in acid solution.

	Fluid meat.				Meat.	Meat extract.
	Rubner.	Less NaCl, Rubner.	Stenhouse and Groves.	Stenhouse and Groves, less NaCl.		
N in dry substance..	10·36	—	11·68	—	14·10	10·25
Ditto, less NaCl....	—	11·86	—	13·36	—	—
Alcohol extract	43·30	—	11·80	—	6·66	70·39
Ash	18·64	—	—	—	—	—
Organic matter	81·36	—	—	—	—	—
N p. c. in organic matter	12·73	—	14·50	—	14·91	13·21

The wide difference between the amounts soluble in alcohol found by Rubner and by Stenhouse and Groves is pointed out, *e.g.*, 43·3 per cent. and 11·8 per cent. The author then remarks that the precipitate of peptone and phosphotungstate is readily soluble in slightly alkaline sodic phosphate, and that peptone, whilst insoluble in absolute alcohol, is soluble to a considerable extent in slightly diluted alcohol, and hence the amounts of soluble and insoluble matter depend very greatly on the strength of the alcohol used. Rubner says that 100 parts of dry fluid meat should contain 91 parts of peptone—but 32 parts of lean meat yield 24 parts of water and 8 of dry substance, and this latter 7 parts of proteids and 1 of extractives, or 87·5 per cent. and 12·5 per cent. respectively, and it is absurd to suppose that 87·5 parts of proteid can yield 91 parts of peptone. Commenting on Rubner's statement that a part of the sodium tungstate precipitate is due to extractives, the author says that such is not his experience, and that although the ordinary *extractum carnis*, so-called, does yield a precipitate, the solution obtained by extracting meat with cold water, and subsequent complete removal of the albuminoids, will not give a precipitate. W. N.

Fluid Meat. By RUBNER (*Zeitschr. f. Biol.*, 16, 212—214).—This is a criticism of the previous paper. Analyses of a second sample of fluid meat are given, which approximate very closely to those of Stenhouse and Groves, of which the author remarks that it is open to objection, as being an analysis of the dry substance and not of the original material. W. N.

Elimination of Nitrogen from the Animal Body. By GRUBER (*Zeitschr. f. Biol.*, 16, 367—410).—The author opens his paper with a recapitulation of Voit's conclusions as to the balance between the nitrogen of the ingesta and that of the excreta of Seegen, and Nowak's objections thereto, and he points out the great importance of the methods used for the estimation of the nitrogen, and proceeds to discuss these at very considerable length.

The method of combustion with copper oxide is first considered,

and examples of its accuracy as illustrated by urea and tyrosine are given. The errors attributed to the method by Kreusler, viz. (1), the air contained in the material used to evolve the carbonic anhydride; (2), the hydrogen condensed on the surface of the reduced copper; (3), the air which obstinately adheres to the walls of the tube; (4), the volatile carbohydrates which in traces escape combustion, are discussed, and there then follows a very lengthy description of Dumas' method as carried out by the author.

The soda lime method is then described and discussed, and illustrations of its accuracy in the case of urea and tyrosine given. The author is of opinion that the objections of Makin that ammonia is dissociated by soda-lime at high temperatures does not apply, as the tubes ordinarily used for combustions are not nearly long enough for this to take place. The importance of the admixture of sugar is pointed out, and as an example analyses of guanidine platinochloride are given, with sugar 6.198 per cent. nitrogen was obtained, without sugar 1.629 per cent. Kynuric acid gives most untrustworthy results. The real question is, however, its applicability to albuminoids. A long table of the results of analyses of meat and pea meal by the two methods is given, in which the difference of the means only once reaches the first place of decimals.

The necessity for exceedingly fine pulverisation is pointed out; examples illustrating the results of neglecting this precaution are given, and the author suggests that Seegen and Nowak's figures may be the result of this neglect.

Then follow a series of tables of the results of experiments on a dog of 17.5 kilos. weight fed on a daily ration of 400 grams of flesh meal and 180 of bacon, and 200 c.c. water. The meat was prepared in large quantity and carefully mixed and sampled, and sufficient for several days being prepared at once and kept in ice, analysis of a piece taken at random, and a sample of the finely divided material (from a large quantity) showed almost identically the same nitrogen value.

Voit's method was used in estimating the nitrogen; the author finds that there is no risk of loss by drying at 100° C. With care, much time is saved by not drying in a vacuum.

A table is given showing the results obtained by Voit and Dumas' method respectively: the difference of the means is very slight indeed. The composition of the meat at various periods is also given. Then follow a series of tables showing the relations of the nitrogenous ingesta and egesta.

I. Period. Ingesta, Dumas	154.81
Soda lime ..	154.14
Egesta, Voit	155.02
II. Period. Ingesta, Dumas.	213.72
Soda lime ..	213.06
Egesta, Voit	213.26

The results of a third experiment show the same close approximation to a balance. An investigation of the sulphur of the excreta shows that the ratio of sulphur to nitrogen in the excreta was

1:16.69, in the food 1:16.72, total sulphur of food 12.77, of excreta 12.78 grams. The author then proceeds to calculate the nitrogen and sulphur of the excreta as meat, and finds that over a period of 10 days the nitrogen accounts for 5,986 grams, and the sulphur for 5,998 grams, out of 6,000 grams actually taken. Comparisons are given of Liebig's method with the others, and the author sums up the results of his investigations under the following eight heads:—

(1.) Schneider's modification of Dumas' method is absolutely accurate.

(2.) The soda-lime process in the majority of cases used after the Will-Varrentrap method gives very accurate results.

(3.) The Will-Varrentrap method is reliable in the analyses of meat and peas.

(4.) Voit's experiments on a pigeon is proved thoroughly correct, Seegen and Nowak's objections notwithstanding.

(5.) From the author's experiments, it is proved that the nitrogen of the food is and can only be found in the tangible excreta.

(6.) The mean nitrogen value of meat (3.4 per cent.) and Liebig's method of estimating nitrogen are, regard being had to the limits of error set out by Voit, practicable.

(7.) Voit's earlier researches on the nitrogenous equilibrium of a carnivorous animal are confirmed.

(8.) Seegen and Nowak's assertion that nitrogen was eliminated from the body in the gaseous form has no foundation in fact.

W. N.

Influence of Borax on the Decomposition of Proteids. By GRUBER (*Zeitsch. f. Biol.*, 16, 198—202).—The experiments were made on dogs fed upon a purely flesh diet. The first series failed, in that on the day on which about 15 grams borax was given, the dog took 100 grams less meat than on the previous days. The urea elimination was notwithstanding not less, and there was reason even to believe that a slight rise in the proteid metamorphosis took place. In the second series, the urea elimination rose from 80.67 grams to 85.25 grams, and amounted on the two following days to 80.78 grams and 81.05 grams respectively. The author hence concludes that borax has some slight influence in raising the amount of proteid metamorphosis.

W. N.

Formation of Urea from Ammonia Salts of Organic Acids. By FEDER and VOIT (*Zeitschr. f. Biol.*, 16, 179—197).—The authors deemed it important to repeat the experiments of Hallervorden on the effects of feeding with ammonium carbonate, on the ground that no precautions were taken in them to control the amount of proteid metamorphosis, and to this end they made use of Salkowski's plan of estimating the total sulphur eliminated not only in the urine but also in the faeces.

The first experiment was made upon a dog 29.7 kilos. in weight, in which nitrogenous equilibrium was maintained on a diet consisting of 550 grams meat and 150 grams bacon. After a fast of 24 hours, the dog took on the 4th day of the experiment 9.9 grams ammonium acetate, which from analysis yielded 1.69 gram NH_3 . On the days

when the normal diet was given, the relation between the sulphur and nitrogen eliminated was as 1:16.28; on the days when ammonia was given 1:18.09 (the nitrogen was estimated by Seegen's method).

This rise indicated that the origin of the nitrogen eliminated was not altogether due to decomposition of proteids, but to something else. Urea and ammonia are the only heads under which the eliminated nitrogen need be considered. The ammonia of the urine shows no appreciable increase after ingestion of ammonia salts, and hence the authors conclude that urea may be and is formed from them in the animal body.

A second experiment was made with ammonium carbonate, the animal being fed as before upon flesh and bacon. On the seventh day of the experiment, after a previous 24 hours' fast, the animal took 20.8 grams NH_3 . On two days of normal diet, the ratio of the sulphur to nitrogen in the excreta was 1:16.25; on the seventh day, it rose to 1:20.8 under the influence of ammonia. The increase in the ammonia eliminated was very slight, and consequently the great bulk of the ammonium salt must have been converted into urea. The expired air examined by means of v. Pettenkofer's apparatus proved to be free from ammonia.

A third experiment was undertaken in order to investigate the importance of two possible sources of error. Firstly, since the nitrogen of the faeces was estimated after drying, it was thought possible that some of the ammonia escaped in the process, and that therefore the results might be too low. Secondly, the amount of ammonia found in the urine might be too low in consequence of its containing too small a quantity of chlorides. By means of a series of control experiments in which at one time ammonium chloride, and at another ammonium carbonate, were added to urine, the quantities of potash and ammonia in which had been most carefully estimated, the authors arrived at the conclusion that when platinum chloride prepared with great care and as free as possible from acid was used, errors to the extent of 18.9 per cent. might occur in the case of urine to which ammonium carbonate had been added, but that under ordinary conditions if the usual solution containing an excess of acid were used and a little alcohol and ether added, very consonant results may be obtained.

In the third set of experiments with 20.94 gram ammonium carbonate, in which the nitrogen was estimated in the fresh faeces, the ratio of sulphur to nitrogen in the normal period was found to be 1:15.08, and in the ammonia period 1:17.61. The ammonia elimination was only slightly higher than normal. These experiments then confirm the statement of Hallervorden that in dogs ammonium carbonate is converted into urea, and further prove that ammonium acetate undergoes a similar change.

W. N.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Temperature on the Germination of Bunt Spores. By F. SCHINDLER (*Bied. Centr.*, 1881, 824). Fungoid growths when dry are capable of withstanding higher temperatures without detriment to their germinating powers, than if exposed to the same temperature in the moist state; the spores of bunt (*Tilletia caries*) has the same property, for they germinated when heated in the dry state to 50°, 65°, 80°, 95° and 100°, after 4, 6, 8, 8 and 10 days respectively, while a duplicate which was not heated germinated in four days. When, however, the spores were moist, and heated to 30°, 35°, 40°, 45° and 50°, germination occurred after 4, 4, 5, 5 and 10 days respectively, the duplicate (not heated) germinated after four days. Cold (—22°) merely delays germination, and does not diminish its intensity.
E. W. P.

The Loss which Newly Mown Grass Suffers when exposed to Rain. By A. EMMERLING (*Bied. Centr.*, 1880, 826—828).—The grass freshly cut was exposed to two falls of rain, and to a third fall after fermentation had set in.

The analyses of the rain water which had fallen on the grass showed that the first rain dissolved out a larger quantity of mineral than of organic matter; the loss in organic matter consisted chiefly of non-nitrogenous material; the amides and nitrates are the most easily removed of the nitrogenous constituents; albumin appears only to be removed after fermentation has commenced; of the mineral constituents, chlorine and phosphoric acid are removed in largest quantities; fermentation greatly aids the solution of the constituents of the grass.
E. W. P.

Cultivation of Potatoes, Maize, Oats, and Sainfoin. By P. P. DÉHÉRAIN and others (*Bied. Centr.*, 1880, 795—800).—*Potatoes.*—The manuring of the potatoes on fertile soils—like those of Grignon—is not productive of any great gain.

Maize.—Stable manure appears to be the best for maize, and for two reasons; it is the source of the nitrogen, phosphoric acid, and carbonic anhydride, and by reason of porosity water is retained by it during dry seasons; also the large amount of humus that it contains directly available for the plants, makes it vastly superior to the ordinary artificial manures. In support of this hypothesis, the amount of carbonic anhydride as carbonates, and as carbonates and organic matter, was estimated in the plots which had not been manured during 1878–79, but in the years 1875–77 had been manured with farmyard manure, or with ammonia salts and nitrates; it was found that the soil became richer in carbonates, but poorer in organic matter, and that the organic carbon was much greater in those plots manured with farmyard manure.

Oats.—The experiments on oats during the years 1876–79, show

that during the season of 1878 the manures had a greater influence on the yield of straw than on the grain, whilst during 1879 the opposite was the case. The average result of the five seasons is, that the influence of manures on oats is but small; the climatic conditions are more influential than manures, especially at the time of blossoming and ripening.

Sainfoin.—Off the land on which the sainfoin was grown, three crops of turnips and one of maize had been taken, and the sainfoin was sown without any additional manure than that which remained in the soil manured by the previous crops; it was found that those plots where farmyard manure had been ploughed in, yielded the heaviest crops, then those manured with sodium nitrate; and the highest crop was taken from the plot which had been top-dressed with farmyard manure.

E. W. P.

The Influence exerted on the Growth of Potato and Jerusalem Artichoke Plants by allowing the "Sets" to decay before Planting. By C. KRAUS (*Bied. Centr.*, 1880, 821—824).—It was sought to determine to what extent the yield of a crop of potatoes (Proskauer-Bisquit) would be influenced when the tubers employed, as sets, were fresh, slightly decayed, and much decayed. The shoots from the fresh tubers appeared first above ground, and the stems produced from large tubers were higher than those produced from small "sets"; and whereas this difference with fresh tubers is less remarkable as growth proceeds, in the case of a decayed "set" the difference is more remarkable, and is in favour of the larger tuber. In all cases, the plants from large "sets" blossomed first, and if the weather is dry, the bloom is most abundant in those plants from the decayed tuber. Small "sets" produce a large number of stems; likewise do also large "sets," which are slightly decayed; in fact, the decay of the small tuber reduces its power to produce stems. The number of tubers produced from decayed sets is greater than that from fresh sets, and so much the more the greater the extent to which the decay had proceeded, and in dry seasons the number of small tubers is also larger. The power of production possessed by any single stem is the higher the more the "set" (from which that stem is produced) is decayed.

The results with Jerusalem artichokes are of the same character as those obtained with potatoes.

E. W. P.

Examination of Various Soils and Subsoils. By C. SCHMIDT (*Bied. Centr.*, 1880, 786—793).—The soils examined were obtained from the neighbourhood of the Black Sea, and were collected at depths varying from 1 foot to 3 ft. 8 in. The results obtained were, that the proportion of alumina to potash and soda is the measure of the decomposition of the felspars present; the smaller the amount of alkalis present, so much the greater is the extent to which the orthoclase and plagioclase has been decomposed; the higher the amount of humus, and the greater the depth in the soil at which it is found, so much the poorer is the soil in alkalis. Excess of humus causes a diminution of the amount of calcium carbonate, by reason of the presence of water highly charged with carbonic anhydride.

E. W. P.

Phosphoric Acid in the Soil. By KOSTITCHEFF (*Bull. Soc. Chim.* [2], 34, 341—342).—The generally received opinion is, that the phosphoric acid in the soil exist as ferric and aluminic phosphates, and that all other phosphates are ultimately converted into these two. The author finds, however, that ferric and aluminic phosphates decompose calcium carbonate in presence of water, with disengagement of carbonic anhydride. He supposes phosphoric acid to be first liberated by the action of water on the ferric or aluminic phosphate; this phosphoric acid then decomposes a portion of calcium carbonate, liberating carbonic anhydride, which dissolves another portion of calcium carbonate. This decomposition takes place even in mixtures containing an excess of ferric oxide over ferric phosphate. J. M. H. M.

Decomposition of Phosphorite by Peat. By BELETZKY (*Bull. Soc. Chim.* [2], 34, 348).—The author has observed results differing considerably from those of Eichhorn. He finds that the presence of salts such as NaCl, Na₂SO₄, KCl, K₂SO₄, CaSO₄, NH₄Cl, (NH₄)₂SO₄, exercises no sensible influence on the decomposition of phosphorite by peat. The presence of ammonium carbonate favours the decomposition. J. M. H. M.

Influence of Sodium Nitrate on Absorption of Phosphoric Acid and Potash. By FIEDLER (*Landw. Versuchs.-Stat.*, 26, 135—165).—One of the properties ascribed to nitrates in the soil is that of facilitating the absorption and assimilation of insoluble matters, and it is asserted that the danger exists, by the employment of such salts as manures, of dissolving and removing from the soil such nutritious constituents, their solutions being washed into the subsoil before they can be taken up by the plant. The evidence of their solvent action has, however, not been proved by many experiments, the assertion resting chiefly on experiments of Liebig reported in the *Annalen*, 105. The author undertakes the present series of investigations to obtain answers to certain questions which he formulates. Firstly, *Do nitrates dissolve out any considerable quantities of plant foods from the soil?* The first series of experiments were intended to ascertain whether a longer or shorter period of digestion of soil in plain water would affect the rate of solution of phosphoric acid and potash. It was found that in three trials, lasting for 1, 12, and 24 hours, the solubility of the phosphoric acid increased, but that of potash diminished. The next experiment was on the effect of nitrate solutions of different strengths acting for 12 hours, but less quantities of phosphoric acid and potassium were dissolved than in the clear water. The author believes his first question answered in the negative.

The second question proposed is: *Does sodium nitrate prevent the absorption of potash and phosphoric acid when present in the same mixture?* As in the former case, the effects of plain water were tried on a mixture containing both salts during one and six hours respectively, but the results were negative. The term of six hours was chosen as the period for experiments with solutions of nitrates of various strengths, and from them it appeared that within certain limits

the absorption is increased proportionally to the strength of the solution; but the experiments could not be carried out to their full extent, as the operator wished to confine himself to such limits as might be met with in actual practice. He however declares that the answer to the second question is, that within those limits the absorption of phosphoric acid is *favoured* by the presence of sodium nitrate, whilst the absorption of potash is slightly impeded.

Thirdly. *Does sodium nitrate convey the phosphoric acid and potash into the subsoil?*

In order to determine this, the author filled a glass vessel with a mixture of the soil to be examined and well-cleansed quartz sand to the depth of half a meter. The bottom of the vessel was contracted and provided with a loose plug of asbestos, a caoutchouc cork, glass tube, and pinch-cock, in connection with a Bunsen exhaust pump. The solutions experimented with were left in contact with the soil during a night in each case, the earth washed carefully, and the phosphoric acid and potash estimated.

The answer given by the whole series was, phosphoric acid is *not* carried into the subsoil through the influence of Chili saltpetre. It is in a certain measure decomposed by the action of the sodium nitrate on the calcium phosphate present in the soil, but it is immediately re-absorbed, and the process continues as long as there is any sodium nitrate present. Potash, however, *does* dissolve, and is carried into the subsoil in the presence of sodium nitrate, but its removal is considerably retarded by the presence of large quantities of lime in the soil; the presence of the lime does not prevent the beneficial effects of the nitrate on the phosphoric acid.

The results of the preceding investigations induced the author to undertake an extended series of experiments on the solubility of various combinations of phosphoric acid with sodium and calcium. Although of little practical value in their present state, there are some deductions which may be usefully drawn from them.

In all the experiments, the presence of sodium nitrate caused a larger amount of calcium and less phosphoric acid to pass into solution than when water alone was employed; that Chili saltpetre does not exert a seriously solvent influence on *tribasic* phosphate, but that it does so affect *dibasic* phosphate of lime, iron, and alumina, and that the influence of heat assists the reactions.

The experiments confirm in general the conclusions drawn by Liebig in his investigations on dibasic phosphate, but the author thinks that the fear expressed by Liebig of the disappearance of phosphoric acid from the soil through the employment of sodium nitrate is exaggerated, his experiments having been conducted under conditions which do not frequently occur in practice.

Many of the author's experiments have an important bearing on the employment of so-called retrograded phosphates, and go to show that their use, combined with sodium nitrate, is of as great utility as that of the superphosphate, and that the prejudices against their use on the ground of their imperfect distribution in the soil and insolubility are unfounded when sodium nitrate is present.

J. F.

Potassium Salts as Manures. By A. MEYER (*Landw. Versuchs.-Stat.*, 26, 77—134).—A prize competition instituted by Liebig was the cause of the author entering on these investigations. He withdrew from the contest from inability to complete his researches in time, but having examined the subject exhaustively, he publishes the results.

The uncertain effects of Stassfurt salts, when employed as manures for beets and clover, has been a subject of frequent speculation and is of importance. The author has been led to form a theory of his own on this subject, which he develops in this paper, and which he thinks will account for many of the irregularities in the working of mineral manures, and of Stassfurt salts in particular.

The theory is, that the food of plants requires to be presented to them in such a form that the bases bear a larger proportion to the acids than is generally the case in mineral manures, and that such manures as are at present manufactured contain large proportions of strong acids, which, when set free by decomposition, are either useless or injurious to the growing plant; and that the difficulty of assimilating those acids is the cause of the frequent failure of Stassfurt salts. He assumes three things as necessary for the proof of his theory: first, that the ashes of all plants are of an essentially basic character; secondly, that all fertile soils offer to plants their food in a suitably mixed condition; and thirdly, that many mineral manures, and notably Stassfurt salts, alter those relations. He gives several examples in which the proportion of bases to acids in the ash is on an average 3 to 1, some of them being as high as 5 to 1, and in tobacco ash as high as 11 : 1 (E. Wolff).

The acids present in the ash of plants are sufficient to saturate only a very small portion of the bases, and if we wish to account for their state in the plant during life, we must conclude that they are in combination with organic acids, oxalic, tartaric, citric, malic, &c. Attempts have been made to cause plants to assimilate mineral acids to an abnormal extent, and they have been partially successful, so far as to yield an acid ash, but at the expense of the health of the plant, as in every case it drooped and died. Experiments on the growth of plants in water and in sand are often likely to lead to false conclusions, as in the actual soil silicates and humates, which play alternately the parts of bases and acids, modify the results of such experiments. Nobbe, in experiments with several nutritive solutions, has declared that potassium chloride is the most valuable manure for buckwheat, but the author contends that the success of his solutions was rather due to the manner in which the bases and acids were divided, the successful ones having a larger proportion of the former. He notices other experiments of Hässelbarth on culture of wheat in sand, wherein two solutions were used; one of ammonium salts, and the other of nitrates. The latter gave the best results, except when the first received an addition of calcium carbonate.

The second proposition of the author is, that a fruitful soil, although not itself strongly basic, enables plants to assimilate bases, and to yield a strongly basic ash. Fertile soils do not consist merely of an earthy skeleton plus nutritive solutions; there are silicates and humates,

which, according to the theory of Grandeau, play a most important part. The author thinks it would not be far from truth to say, that an ordinarily fertile soil contains, among its insoluble constituents, calcium carbonate, tribasic calcium phosphate, aluminium silicate, ferric oxide, lime, potash, magnesia, and ammonia, in combination with humus, &c., &c. Soils which have been tilled for a long time become even more complicated in their structure, containing unknown combinations of humus with bases and acids, Grandeau's *matière noire*, &c., whilst in the soluble portion of the soil are found calcium nitrate, potassium sulphate, sodium chloride, alkaline humates and silicates, a little carbonate of calcium and magnesium, and possibly gypsum. The nutritive matters are taken up from the soluble portion without chemical change, the roots of the plant having apparently the power of absorbing even solid particles; the strong organic acids present in the plants prove to be important agents in the absorption of the bases, the calcium carbonate present in the soil neutralising the liberated mineral acids and forming again neutral chlorides, sulphates, and nitrates of the alkalis. The value of farmyard or stable manure is enhanced by its ash being naturally of a basic character, similar to that of plants; the decomposition of the albuminoid constituents into ammoniacal compounds, and the absence of organic acids preserve its basic character, and where such organic acids are present, they moderate the extreme alkalinity; but the chief work is done by the humates and silicates. The presence of calcium carbonate in soils acts as a regulator of the various reactions, and theory endorses the verdict of practice that alternate applications of marl and heavy manuring are beneficial to soils of a clayey or humous character.

The author's third subject of examination is the influence of mineral manures, and chiefly Stassfurt salts on soils. In his opinion, as before stated, the value of an artificial manure depends on the strength or weakness of combinations of the acids and bases contained therein, and the facility with which they are dissociated. The dissociation is easiest with nitric acid and ammonium compounds, from which proteid matters are easily formed. Carbonic anhydride too, being so easily expelled from its combinations by strong vegetable acids, is of great value. Sulphates come next, but at a distance behind the others. Hydrochloric acid compounds, however, do not possess any of these desirable properties.

The author divides all mineral manures, according to the foregoing ideas, into three broad divisions, viz., salts whereof the bases and acids are alike easily absorbed by the plant: these he calls physiologically neutral. Salts of which the bases are absorbed more easily than the acids, called physiologically acid. Salts of which the acids are more readily assimilated than the bases, called physiologically basic. In the first group he places calcium and magnesium sulphates, sodium chloride, superphosphates of lime and ammonia, dissolved Peruvian guano and potassium nitrate. In the second, ammonium, potassium, and magnesium chlorides, ammonium and potassium sulphates, superphosphate of potash, and Stassfurt salts in general. In the third group are found calcium and potassium carbonates, calcium phosphate (without sulphuric acid), commercial sodium

nitrate, raw guano, bone meal, wood ashes, and caustic lime. Amongst general conclusions arrived at are, that manures of the second class are those which are dangerous, if not actually hurtful, to vegetation. Ammonium sulphate, notwithstanding its facility of absorption, is less useful, especially in soils poor in lime, than its equivalent of Chili saltpetre. Calcium diphosphate works better in such soil than superphosphate made with acid, provided the same quantity of P_2O_5 be present. The chlorides of the different bases are of less value than the sulphates, some small portion of the latter acid being assimilable. Briefly, all acid manures, in comparison with their contents of plant-food, are bad—all neutral are useful, but the most valuable of all are to be found in the third or physiologically basic class.

The author quotes various experiments of his own, and of other observers in the same direction, in proof of his views—many of them bearing on the preference which should be shown to sulphates over chlorides.

The injurious effects of chlorides has been the cause of the failure of Stassfurt salts, and has caused a great change in the trade of the district. Carnelite, composed chiefly of the chlorides, is being neglected in favour of kainite, which contains more of the sulphates, but even this salt is largely contaminated with the objectionable chlorides, and is of secondary value. The author draws attention to the fact of superphosphates being made with sulphuric instead of the cheaper hydrochloric acid, as a practical proof of the inferiority of manures containing chlorides.

The results of some experiments made with different manures on poor soils will be found interesting.

Crop.	Manure.	Rate of increase.
Beet	Superphosphate	Ninefold.
„	Potassium chloride ..	Two-and-half fold.
„	Potassium sulphate ..	Five-and-half fold.
Potatoes....	Ditto	} Threefold.
„	Potassium chloride ..	
Oats	Various potash salts..	No increase.

Suggestions are made for the addition of various substances to the Stassfurt salts. Wood ashes, which contain large proportions of calcium and potassium carbonates, and is in itself a valuable manure for wheat, clover, and sugar-beets, would prove a valuable addition, but it is too valuable for other purposes to be used as manure, the reason of its value being, in the author's opinion, the favourable proportion of its bases to its acids. Caustic lime added to the salts in question, has undoubtedly a very beneficial effect. It has been recommended by Lehmann, Wolff, Nobbe, and others; but the formation of calcium chloride is one of the evils resulting from this treatment. However, if the manure is put into the ground in the autumn, the soluble chloride formed is dissolved by the winter rains, and sinks to a lower stratum; yet further on, the author cautions against its use, where certain plants are cultivated which are extremely susceptible to the injurious influence of calcium chloride. Experiments are recorded which show an unfavourable influence when

calcium chloride is applied, either directly or in consequence of reactions in the manures, some plants being more sensitive than others in this respect.

Experiments with mixtures of other potassium salts and the chloride were not favourable. Potassium carbonate yields variable results, much depending on the other constituents of the soil; the author pronounces potassium carbonate to be a capricious manure, and greatly inferior to wood ashes. Stable manure, however, by its slow decomposition and formation of carbonates in a gradual manner, being the model of all manures.

Experiments with silicates of potash are given; their manufacture is too costly, and their results too uncertain to encourage experiments in that direction. Attempts were made with combinations of potash with humic acid, by saturating peat with potash-solution, the results were in the main favourable, but not decisive. Trials were made with potassium nitrate, the splendid results agreed with former experiments; but the cost of the manure is so great that its employment is practically impossible, except in special cases, such as the growth of valuable bulbs.

Finally, the author sums up by saying that potassium salts play a minor part in the economy of plant nutrition compared with nitrogen and phosphorus. That their employment requires application in winter to admit of deleterious compounds being dissolved out and washed away, and he recommends that new compounds of potash with carbonic and phosphoric anhydride, humus, and silica should be introduced to farmers, if they are to reap all the benefits to be drawn from Stassfurt salts.

J. F.

Manuring of Cress with Dicalcium Phosphate on Soils Free from Humus. By H. ALBERT and SIEGFRIED (*Bied. Centr.*, 1880, 793—795).—Common cress was sown in a calcareous soil contained in large boxes, and the following manures were applied:—3·65 grams dicalcium phosphate, 36·7 grams phosphoric acid; 3·65 grams dicalcium phosphate, and 8·9 potassium sulphate (30 per cent. K_2O); 8·9 potassium sulphate only; no manure was added in the fourth; the crops were sheltered from rain, but watered with distilled water. The conclusions drawn are: (1) in the absence of humus the plants can absorb phosphoric acid from the neutral compound; (2) manuring with dicalcium phosphate alone, or along with potash, increases the yield; (3) potash and phosphoric acid increase the amount of nitrogen and phosphoric acid present in the plant; (4) potash and phosphoric acid increase the amount of albuminoids.

E. W. P.

Analytical Chemistry.

Notes on Gas Analysis. By M. FILETI (*Gazzetta*, **10**, 1—12).—
In analysis of gases by absorption, the author recommends the use of balls of plaster of Paris, made from a block of the dry plaster, and

having a notch cut round the circumference of the sphere into which the platinum wire, which supports it, may be fitted; these have no absorbent action on most gases.

In saturating a gas with moisture, instead of passing a drop of water up into the eudiometer as recommended by Bunsen, it is far better to employ a plaster ball dipped in water, and the adhering moisture removed by blotting-paper, temporarily diminishing the pressure of the gas; by this method the sides of the tube are not wetted, and the gas can be easily dried and again saturated with moisture, five or six times successfully, without any difficulty.

The author has also made experiments on the action of chromic acid solution on hydrogen and on carbonic acid—a reagent proposed by Ludwig (*Annalen*, **162**, 47) for separating the two gases, as he states that it does not act on the former, but oxidises the carbonic oxide somewhat rapidly. It seems, however, that not only do chromic acid solutions gradually absorb hydrogen, but even concentrated solutions (1 : 2) oxidise carbonic oxide too slowly to allow of its being used as a means of separating the gases, less than half the carbonic oxide being removed from a mixture containing 24·28 per cent. CO after 33 hours' exposure.

C. E. G.

Destruction of Organic Matter when Searching for Metallic Poisons. By A. G. POUCHET (*Compt. rend.*, **92**, 202—204).—From 100 to 500 grams of the suspected matter are mixed in a large porcelain dish with 25 per cent. of perfectly pure potassium hydrogen sulphate, and a quantity of fuming nitric acid, equal in weight to the organic matter taken, is then added. The reaction is at first very violent, but afterwards must be assisted by gentle heating. Pure sulphuric acid of 66° B. is now added in large excess, and the mixture heated nearly to the boiling point of the acid. By long-continued heating, with further addition, if necessary, of sulphuric acid, all the organic matter may be completely destroyed. It is advisable, in order to ensure the destruction of the last traces of organic matter, to allow the liquid to cool, then add a few crystals of potassium nitrate, and again heat until white fumes are given off. In this way a clear limpid liquid is obtained, which solidifies on cooling, and contains, in the state of sulphate, all the metallic elements present in the suspected matter, together with a large excess of sulphuric acid. The saline mass is dissolved in boiling water, and, if 200—300 grams of the suspected matter have been taken, diluted to about one litre. The solution, *without previous filtration*, is then electrolysed by means of four Bunsen's elements, or, preferably, a Clamond gas pile. The electrodes should be of platinum, except when mercury is sought for. In this case the negative electrode should be of gold. By this method the author was able to estimate quantities of lead not exceeding 0·5 mgrm. per 100 grams of organic matter, such as food, urine, or animal organs, and to detect mercury in 200 grams of liver, to which 0·5 mgrm. mercuric chloride had been added. The potassium hydrogen sulphate retains the more volatile elements, such as mercury.

To detect arsenic or antimony, the carbonaceous mass obtained by the first treatment, before adding sulphuric acid, should be boiled

with water and the aqueous solution treated by Gautier's method (*Compt. rend.*, 1875; comp. this vol., p. 311). C. H. B.

Use of the Azotometer for Agricultural Investigations. By A. MORGEN (*Zeits. Anal. Chem.*, 1881, 37—48).—It is known that the estimation of ammonium compounds, by measuring the nitrogen evolved on their decomposition by alkaline hypobromite, is rendered incorrect by the presence of urea and other nitrogenous substances of the amide class which evolve nitrogen under these conditions: the serum of blood, egg albumin, and casein are said also to evolve nitrogen when treated with the mixture of bromine and soda solution. This fact will evidently limit the use of the azotometer; its results will become false when applied to vegetable extracts and many classes of soils, and to blood.

The author has made experiments to test the accuracy of Sachsse and Kormann's method, which consists in heating the vegetable extract with acid until the amides are converted into ammonia and amido-acids, and then estimating the nitrogen as ammonia in one portion by the azotometer, and that present as amido-acids by nitrous acid. It is found that not only do the amido-acids evolve some nitrogen in the azotometer, but that gas is also evolved from other substances, even non-nitrogenous, which are present in the extract, and further by the action of the acid on the bromine solution, even when the acid is not in excess. The error thus occasioned is, however, much reduced by diluting the solution and neutralising the acid.

The conclusions arrived at as regards the use of the azotometer for determining nitrogen present as ammonium salts, are:—

1. That the method gives satisfactory results in solutions of pure ammonium salts.
2. That the presence of nitrogenous organic substances, such as albumin, amides, peptones, ferments, alkaloids, and glucosides, renders the method useless.
3. That the presence, in any considerable proportion, of non-nitrogenous organic bodies, renders the estimation inexact.
4. That for the estimation of ammonia in presence of amido-acids, and many other nitrogenous bodies, the azotometer is altogether unsuitable; the determination of ammonia, separated from bodies of the amide class by the action of acids, by the azotometer, yields very inaccurate results.

F. C.

Estimation of Retrograde Phosphoric Acid by means of Ammonium Citrate. By A. KÖNIG (*Zeits. Anal. Chem.*, 1881, 49—57).—The quantity of substance to be treated with the ammonium citrate solution is different according to different chemists; the author finds that the use of one and two grams gives percentages of phosphoric acid, differing by one-sixth. The degree of alkalinity of the solution seemed to exercise little influence on the result; but the quantity of phosphate dissolved by the same quantity of citrate solution, although increasing as larger quantities of phosphates were employed, did not increase in proportion to the weight of phosphate

used; hence the percentage found always diminishes as the weight of substance treated with the citrate is increased.

It is evident, therefore, that the results yielded by this method are only relatively correct when the same quantity of phosphate soluble in the citrate solution is present in every analysis. Since this is a condition impossible to secure, it is necessary to work always in a precisely similar way, and to state the quantity of substance employed for the estimation, the latter being a point of great importance.

F. C.

Estimation of Soluble Phosphate in Superphosphates. By S. DREWSSEN (*Zeits. Anal. Chem.*, 1881, 54—57).—It is generally considered that by drying a sample of superphosphate some of the soluble phosphoric acid is rendered insoluble, hence the phosphoric acid is estimated in the undried sample. The author attributes the deficiency of phosphoric acid found by precipitation by ammonium molybdate in dried samples, to the conversion of some of the orthophosphoric into pyrophosphoric acid. He finds accordingly that, if before addition of molybdate the dried sample is first boiled after addition of nitric acid, which converts pyrophosphoric acid into orthophosphoric again, the deficiency disappears; this preliminary treatment with nitric acid has the further advantage of rendering the molybdate precipitate more granular, and of causing it to subside more rapidly and to be more readily filtered and washed. Since it is impossible to know whether samples of superphosphates have been artificially dried, it is necessary always to boil with nitric acid before precipitating with molybdate solution.

F. C.

Aluminium Phosphate. By L. L. DE KONINCK and THIRIART (*Zeits. Anal. Chem.*, 1881, 90—91).—Aluminium phosphate is completely soluble in ammonium hydrate, in the presence of excess of phosphoric acid or of alkaline phosphates; hence in such cases on addition of ammonia the precipitate which forms at first rapidly disappears. From such a solution, however, acetic acid reprecipitates the aluminium phosphate. Arsenic acid and alkaline arsenates behave in a precisely similar manner in presence of aluminium salts. This observation has also been made by Rivot.

F. C.

Determination of Phosphorus in Iron and Iron Ores. By VON EGGERTZ (*Chem. News*, 42, 87).—Korschelt in describing a process for the estimation of phosphorus, makes some observations against the author's method, and proposes several improvements on it. The following are said to be the chief objections, which cause much trouble in practice:—

1. The evaporation of the iron solution before precipitation.
2. The time required for precipitation (two or three hours).
3. Drying at 95° demands much time. It was found that where speed is necessary, the iron as well as the molybdate solutions may be previously warmed to 40°, which shortens the time required for precipitation to one or two hours. By drying the precipitate at 120° to 140°, the alteration which takes place is unimportant, and merely

affects the third or fourth decimal if the amount of phosphorus is not very large.

4. As ammonium phosphomolybdate loses ammonia in drying at a constant temperature of under 100° , Korschelt substitutes a solution of potassium molybdate for the precipitation of phosphoric acid, and thus avoids the tediousness of the author's process of precipitation and drying.

The author raises similar objections to Korschelt's process, and concludes that his own process demands no more labour and little more time than Korschelt's method. By collecting the precipitate in a funnel tube, pressing it together, and measuring, as described in the process, small amounts of phosphorus can be estimated in a much shorter time.

Rammelsberg finds that the amount of phosphorus in the precipitate of potassium phosphomolybdate must be taken at 1.768 instead of 1.73 per cent. if obtained from an iron solution, and at 1.847 per cent. if from a solution free from iron.

Finkener says "from what Korschelt prescribes, that in an iron containing 0.1 per cent. phosphorus, none will be found present."

Riley communicates in this Journal (33, 104) the magnesia method used by him for the estimation of phosphorus in iron.

In comparing this method with that of the author, it is found:—

1. That with reference to precision in weighing the precipitates, we require to use seven times greater amount of iron (17 grams), because the ignited pyrophosphate of magnesia contains 27.95 per cent. of phosphorus, but the phosphomolybdate of ammonia only 1.63 per cent. phosphorus.

2. That the magnesia method demands much more time, labour and skill.

3. That besides nitric acid, the author uses no other reagent which can contain phosphoric acid, whilst Riley uses a magnesium salt, citric acid, also sodium acetate and sulphite. These last-named reagents are exceedingly difficult to procure completely free from phosphorus. It is thought that in this circumstance lies the explanation that Riley, as he says, often obtains about 0.02 per cent. higher phosphorus in iron than several other chemists.

D. B.

Varying Condition of Carbon in Steel, and its Influence on Eggertz's Coloration Process. By J. S. PARKER (*Chem. News*, 42, 88).—Although Eggertz's coloration process for the estimation of carbon is universally adopted in the laboratories of steel works, most chemists have occasionally noticed anomalous results, which have aroused suspicions as to its trustworthiness. After a thorough investigation, the author found that it was liable to great variations. A number of experiments with different samples of crucible and Bessemer steel of various tempers was made, and by observing the phenomena when the cold nitric acid was added to steel drillings, and by numerous check estimations by combustion or chromic acid oxidation, the author became convinced that carbon was capable of existing in steel in different conditions, and that steel containing the same percentage of carbon might give, when dissolved in nitric acid, a

greater or less degree of coloration, according as the carbon was in one condition or another. The author was able to apply a method of correction, which, although entailing additional trouble, rendered the process in all ordinary cases susceptible of a high degree of accuracy. He has not yet sufficiently determined the exact nature of the differences in condition of the carbon giving rise to the various phenomena observed, but thought it right to draw the attention of chemists to a source of variation in the coloration process, which, if not duly corrected, most seriously affects its accuracy; a source of error which has hitherto escaped detection. D. B.

Separation of Copper and Zinc by Precipitation with Sulphuretted Hydrogen. By G. LARSEN (*Dingl. polyt. J.*, 239, 239).—Referring to a former notice (*ibid.*, 229, 302) on this subject, the author mentions that the separation of zinc from copper is easily performed, but it is necessary to precipitate from a hot solution and wash with warm dilute hydrochloric acid (sp. gr. 1.05) saturated with hydrogen sulphide, and then with water to remove the excess of acid. Contrary to the usual assumption, it was found that zinc is not precipitated along with copper by sulphuretted hydrogen in a solution strongly acidified with hydrochloric acid. As to the further treatment, the author finds ignition with pure sulphur in a current of hydrogen the most suitable and accurate method. D. B.

Estimation of Arsenic as Magnesium Pyroarsenate. By F. REICHEL (*Zeits. Anal. Chem.*, 1881, 89—90).—Instead of igniting the precipitated magnesium ammonium arsenate in oxygen, or drying at 105°, the author recommends the following method. The precipitate is removed from the filter into a watch-glass; the filter-paper is then wetted with solution of ammonium nitrate and dried, and incinerated in small pieces in a porcelain crucible; the precipitate is introduced into the crucible moistened with nitric acid, carefully dried, and ignited strongly for 10 minutes. The results are very exact. F. C.

Use of Baryta to obtain Metallic Arsenic from Arsenious Oxide and Arsenic Sulphides. By C. BRAME (*Compt. rend.*, 92, 188—189).—In order to obtain metallic arsenic from arsenious oxide in toxicological investigations either potassium cyanide or black flux is usually employed. Both these substances are deliquescent, and generally give off water on heating, thereby frequently cracking the tube. Powdered baryta gives off no water, and is a much more convenient reagent for the purpose. With arsenious oxide it forms metallic arsenic and barium arsenate. The latter may be dissolved in nitric acid and tested for arsenic acid by means of silver nitrate. The sulphides of arsenic also yield metallic arsenic when heated with baryta.

When chlorine is allowed to act on the rings of arsenic obtained with the modified form of Marsh's apparatus, arsenic pentachloride is formed, and this, when exposed to the action of the aqueous vapour

in the air is decomposed with formation of hydrochloric and arsenic acids. The latter may be detected by means of silver nitrate.

C. H. B.

Quantitative Determination of Silver in Galvanic Silver-baths. By F. MARECK (*Dingl. polyt. J.*, **239**, 240).—The author refers to a recent proposition made with regard to the quantitative determination of silver in galvanic baths by precipitation with sulphide of ammonium. He states that in 1861 he had occasion to study this question, when he worked out the following method:—100 c.c. of the silver-bath are treated with sulphide of ammonium, which deposits silver in the form of a black precipitate, readily separated from the supernatant fluid. The precipitate is thrown on a filter as rapidly as possible, and washed with hot water, and a small quantity of sulphuretted hydrogen water. It is then transferred to a flask, dissolved in nitric acid and titrated with a decinormal solution of sodium chloride. The author worked with baths containing large quantities of cyanide of potassium, and found that this method gave accurate results.

D. B.

Estimation of Carbonic Anhydride in the Air. By A. MUNTZ and E. AUBIN (*Compt. rend.*, **92**, 247—249).—The authors have devised the following method with a view to determine:—(1.) Whether the proportion of carbonic anhydride in the air in a given region varies considerably, or whether the variations are insignificant. (2.) Whether the carbonic anhydride is concentrated in the lower layers of air, or is uniformly diffused. Tubes similar in form to those used by Regnault for collecting air, are filled with fragments of pumice previously ignited with sulphuric acid, and introduced into the tubes whilst still warm. The pumice is then saturated in an atmosphere free from carbonic anhydride, with a measured volume of a solution prepared by dissolving 1 kilo. of caustic potash in 1,400 c.c. of water, adding 200 grams barium hydrate, agitating from time to time, and then withdrawing the clear solution, which absorbs carbonic anhydride with great rapidity. It contains a trace of combined carbonic acid, and this gives rise to a slight error, which, however, is the same for all the tubes prepared with the same solution, and may be determined once for all. The tubes containing the pumice saturated with potash-baryta solution are carefully sealed. To make a determination the ends of a tube are broken and a known volume (about 200 litres) of the air to be experimented on is drawn through the tube either by means of an aspirator of known capacity, or by means of a specially constructed and gauged pump. The tube is then sealed, and may be kept for any length of time. In order to determine the amount of carbonic anhydride, one of the ends of the tube is opened, connected with a Sprengel pump, and the tube rendered vacuous. Dilute sulphuric acid is then allowed to enter at the other end, and the carbonic anhydride evolved is extracted by means of the pump, collected in a graduated tube, and its volume determined by absorption with potash.

Direct experiment has shown that the process gives accurate results. One tube is sufficient to absorb every trace of carbonic anhy-

dride from the air if the latter be not passed through at a greater rate than 4 to 5 litres per minute. By means of this method, determinations of carbonic anhydride may be made in regions in which other processes would not be practicable. The aspiration of 200 litres of air may be accomplished in less than an hour, and by persons unaccustomed to delicate manipulation. C. H. B.

Apparatus for Testing the Inflammability of Petroleum. By C. ENGLER and R. HAASS (*Zeits. Anal. Chem.*, 1881, 1—36).—From a series of trials of the various forms of apparatus invented for this purpose, the results of which are given in detail, the authors draw the following conclusions:—

1. The quantity of the sample employed for each trial must always be the same, and a fresh portion must be taken for every trial.

2. In the process of heating, the petroleum must be slowly and uniformly heated throughout.

3. The oil must be raised in temperature at least 10° C. before it reaches its flaming point: hence it will sometimes be necessary to cool the sample artificially, before commencing the test.

4. The igniting flame or spark must be always of the same size and intensity, and must be at the same distance from the surface of the oil, care being taken that it never comes so near or acts so long as to heat the surface.

5. The object of the test renders it necessary to imitate as nearly as possible in the test-apparatus the conditions of the formation of vapour in petroleum lamps.

It will be seen that the method of agitation has distinct advantages over others, since it does not require either the use of the same quantity of oil, or the distance of the source of ignition from the surface to be invariable; and the difference in the rate of heating has but small influence on the result.

The conclusions arrived at with regard to the different forms of apparatus in use are as follows:—

1. All those which measure the tension of the vapour are to be rejected, since no simple relation exists between vapour-tension and inflammability.

2. If the petroleum is contained in an open vessel, the results are too high and variable to insure even approximate accuracy.

3. The apparatus of Tagliabue, Sintenis' pyrometer, and Parrish's naphthometer, although closed, give results too variable to be trustworthy.

The apparatus of Bernstein and of Abel give concordant results, the former somewhat too high and the latter too low.

The most exact and constant results were obtained with the two closed electrical apparatus, the nearest approach being also made in these to the conditions of vaporisation in a lamp: they further presented the advantage of being but slightly affected by the varying conditions of use already enumerated. Unfortunately the costliness and fragile nature of these forms of apparatus render them unsuitable for any but trained hands.

The improved naphthometer of one of the authors, which depends

on Victor Meyer's principle of agitation, comes next to the electrical apparatus in accuracy, and of all the forms of apparatus described is the least dependent on conditions. Its simplicity of construction, cheapness, and handiness recommend it for ordinary use above all others.

F. C.

Remarks on the Properties of Vapours of Chlorinated Organic Compounds. By BERTHELOT (*Compt. rend.*, 92, 267—268).—The presence of volatile chlorides, such as chloroform in blood and similar liquids, is detected by passing their vapour mixed with air and water-vapour through a red-hot tube, and leading the gases into silver nitrate solution, when a precipitate of silver chloride is formed. The electric spark, and combustion, have the same effect as the red-hot tube. The presence of hydrocyanic acid and acetylene in the gases introduces sources of error, for the former produces a precipitate even in strongly acid solutions of silver nitrate, and the latter produces a precipitate in neutral or slightly acid solutions. Acetylene is formed if the oxygen present is not sufficient to burn all the hydrocarbons completely; it is formed, for example, when a solvent rich in carbon has been employed for the purpose of extracting the chloroform. Hydrocyanic acid is produced if the hydrocarbons are mixed with only a small quantity of ammonia, such as might easily be given off from a liquid containing animal matter. Under the influence of the electric spark free nitrogen in presence of hydrocarbons is, as is well known, converted into hydrocyanic acid. The formation of the silver acetylide may be prevented by making the silver nitrate solution strongly acid. This, however, does not affect the hydrocyanic acid. It is better to dissolve the gases in pure water, and then boil the latter for some time. The hydrocyanic acid and the acetylene are thus expelled, but the hydrochloric acid remains in solution, since it forms a hydrate, which is less volatile than pure water.

C. H. B.

Estimation of Glycerol in Beer. By F. CLAUSNIZER (*Zeits. Anal. Chem.*, 1881, 58—82).—Glycerol is only present in minute quantity in genuine beer, but is frequently added to impart a full sweet taste and conceal hardness, it also effects a saving in malt. The quantity present may occasionally be abnormally high, from the use of yeast preserved by glycerol, and imperfectly washed. Its addition indicates that the beer is inferior, and requires improving, and the glycerol added may also be impure and injurious.

The author briefly describes and criticises at some length the various methods in use for estimating glycerol in beer. All of them, with the exception of that of Lallieu, which is not trustworthy, are modifications of Pasteur's method, which consists in extracting the glycerol from the residue obtained by evaporating the beer with addition of slaked lime, and drying and weighing it. The solvents employed are alcohol, alcohol and ether, or alcohol and chloroform.

The results obtained by these processes are rendered false by neglect of some of the little known properties of glycerol. The following sources of error are noted:—

1. Since glycerol passes over in small quantity when distilled with water, it is not advisable to use the residue left after distilling off the alcohol for the glycerol estimation.

2. Glycerol undergoes oxidation when mixed with lime and charcoal and exposed to the air, hence sand or powdered marble should be used instead of charcoal to mix with the beer, in order to render the drying and treatment of the residue more easy.

3. At 100—110°, glycerol is sensibly volatile in an open dish, but when heated in a small flask, or in a dish in the drying oven, the loss is very small.

4. Glycerol forms a compound with lime, which is only slightly soluble in alcohol; this compound forms gradually during the drying of the glycerol, when lime is present in excess. To avoid this, the beer should be exactly neutralised with lime, and the residue of evaporation dried over sulphuric acid at ordinary temperatures, since glycerol evaporates from a neutral liquid when heated. Absolute alcohol extracts the whole of the glycerol from a residue obtained in this way, but in a somewhat impure condition.

5. The extraction of the whole of the glycerol from the residue when lime was not added in excess was secured only by treating the residue for some time with hot 88.5 per cent. alcohol in an extracting apparatus; treatment with cold alcohol or ether-alcohol was insufficient. If alcohol alone is used, the dissolved impurities must be removed by subsequent addition of ether. If lime is added in excess, the alcohol must contain water to dissolve the glycerol.

6. In presence of excess of lime, the free alkalis liberated from their phosphates pass into the alcoholic extract, and must be estimated as ash by burning off the glycerol. The free alkali tends to render other substances present in the residue soluble, but this error is avoided to a great extent in the extraction apparatus proposed by the author, since the alkalis are quickly removed.

The author proposes the following mode of estimating glycerol in beer as the most trustworthy. 50 c.c. are evaporated in a dish with a glass rod previously tared; when the carbonic anhydride has escaped, about 3 grams of slaked lime are added, and the whole is evaporated to a syrup, about 10 grams of coarsely powdered marble are then stirred in, and the stirring occasionally repeated during the drying, until hard lumps remain. The dish is then re-weighed, its contents are rubbed to powder, and an aliquot part ($\frac{2}{3}$ — $\frac{3}{4}$) subjected in the extracting apparatus for four to six hours to the action of 20 c.c. of 80—90 per cent. alcohol; the alcoholic extract is mixed with 25 c.c. of dry ether, and after standing an hour it is filtered into a weighed small flask, and the filtrate and precipitate are washed with alcohol-ether (2 : 3). The flask is placed in an oblique position on a gently heated water-bath, until the ether and alcohol are removed, and the residue is then dried in the lightly covered flask at 100—110°, until not more than 2 mgrms. are lost in two hours; the drying occupies from two to six hours. If the ash is to be estimated, the glycerol is rinsed with water into a platinum dish, dried, and incinerated; the ash need rarely be estimated.

The beers usually drunk in the neighbourhood of Wageningen

(Holland) were found to contain from 0.206—0.264 gram in 100 c.c. of glycerol free from ash, the ash varying from 0.030—0.039.

F. C.

Estimation of Nitroglycerol in Dynamite. By W. HEMPEL (*Zeits. Anal. Chem.*, 1881, 82—87).—Saponification with potassium hydrate yields too low results, owing to formation of ammonia and potassium nitrite, whilst titration with normal alcoholic potash gives high results; the only methods of precision hitherto described are either an elementary analysis or the extraction of the nitroglycerol by a solvent, and both these processes are tedious, and do not allow a sufficiently accurate opinion to be formed of the explosive power of the substance.

The author finds that Walter Crum's method gives very satisfactory results, and is rapid in execution. The dynamite is agitated with sulphuric acid and mercury, and the nitrogen estimated as nitric oxide; excess of sulphuric acid retards the reaction. Dynamite is readily soluble in strong sulphuric acid, as are also the first products of the reaction, which are probably glycerol sulphuric acid and nitric acid.

A special form of apparatus is described and figured, consisting of the vessel for decomposition, which can be connected above by capillary tubing with the tube for measuring the nitric oxide evolved, and communicates below with a mercury reservoir by means of flexible tubing. About 0.35 gram of the dynamite is introduced into the decomposition vessel in a small tube, into which 5 c.c. of strong sulphuric acid has been also poured. The air having then been expelled by mercury, the vessel is well shaken until the evolution of gas ceases, the gas is transferred to the measuring tube, and its volume read either in the dry state over mercury, or over water. The determination takes about half an hour. The quantity of sulphuric acid used must not be varied; with less than 5 c.c. the reaction proceeds too slowly, and with more the results are too low.

This method is applicable to gun-cotton and other nitro-compounds. When measured over mercury, the percentage of nitrogen obtained from pure nitroglycerol varied from 18.32 to 18.45, and when measured over water 18.23 was found; theory requires 18.5 per cent.

F. C.

Detection of Salicylic Acid in Urine. By A. BORNTRÄGER (*Zeits. Anal. Chem.*, 1881, 87—89).—Robinet detects salicylic acid by its reaction with ferric chloride after addition to the urine of lead acetate, and precipitation of the lead by sulphuric acid. It is shown by Pagliani that the presence of free mineral acids in any quantity hinders or prevents the reaction, whilst organic acids may also slightly hinder; he recommends, therefore, the addition of ferric chloride to the filtrate from the precipitate caused by lead acetate, and the gradual addition of sulphuric acid until the red colour due to acetic acid just disappears, when the violet coloration due to salicylic acid will be seen. The author has tried whether the lead acetate is best used in the impure or pure condition; he finds that with pure lead acetate the filtrate yields better results, but must be tested at once, as after standing for a time it darkens in colour; 0.002 per cent. of salicylic acid yielded a feeble reaction, and 0.005 a very distinct violet-red colour, changing to violet.

The filtrate from the impure acetate gave a delicate rose-red tint. The colour appeared only after a time, and was permanent for 24 hours, addition of a large quantity of acid did not destroy it. Hence Robinet's method is suitable and delicate; pure lead acetate should be used unless the filtrate is found to darken too rapidly, when the impure solution must be substituted; it is considered better not to omit the preliminary treatment with lead acetate. F. C.

The Acidity of Milk. By E. MARCHAND (*Bied. Centr.*, 1880, 819). Turmeric paper, cochineal, and logwood tinctures will detect 2 per 1000 of lactic acid in milk; or if litmus-paper is employed 2 volumes of neutral 90 per cent. alcohol should be added to separate the casein, which colours litmus light blue.

The editor considers that the acidity of milk is more likely to be due to acid sodium phosphate. E. W. P.

Adulterated Linseed Oil. By A. H. MASON (*Pharm. Journ.*, 1881).—The sp. gr. was found to be 0.9146, that of genuine boiled linseed oil being 0.94. It flashed at 165.5° C.; genuine oil flashes at 282.2° C.

The sample was examined by Thomson's method. After having been saponified with alcoholic soda solution, it was mixed with sand and treated with light petroleum boiling below 87.7° C. The light petroleum, separated from the soap of the vegetable oil, was distilled below 104.4° C., and the residue of mineral oil weighed. It was found that 24 per cent. of mineral oil of 0.872 sp. gr., and 137.7° C. flashing point, had been extracted from the sample. F. C.

Estimation of Tannin. By J. LÖWENTHAL (*Zeits. Anal. Chem.*, 1881, 91).—In employing the author's method for estimating tannin, the mixture of dilute acid with the tannin and glue solutions should be well stirred for five minutes; the solution then filters readily, and yields a perfectly clear filtrate. F. C.

Analysis of Coffee. By F. M. RIMMINGTON (*Pharm. J. Trans.* [3], 11, 529).—Chicory and dandelion may be detected in coffee by treating it with bleaching-powder, after previous boiling with sodium carbonate and washing with water to remove extractive matter. By this means chicory and dandelion are bleached, whilst coffee undergoes little or no change. L. T. O'S.

Test for Quebracho-bark. By G. FRAUDE (*Ber.*, 14, 310—320).—For the recognition of this bark, 5 grams of the bark are boiled with 25 c.c. light coal tar benzene, filtered whilst hot, and the extract shaken with 10 c.c. dilute sulphuric acid. The solution of the sulphates is decomposed with ammonia, and then extracted with ether. The ethereal solution is evaporated, and the residue boiled with perchloric acid, or first add water, then three or four drops of concentrated sulphuric acid and the smallest possible quantity of potassium chlorate, and boil. In both cases, an intense coloration resembling fuchsin is obtained. This coloration is due to aspidospermine, and the solution may be further examined by the spectroscope. P. P. B.

Technical Chemistry.

Rendering Furnace-gases Inactive. (*Dingl. polyt. J.*, **239**, 215—219).—Freytag proposes to absorb the sulphuric acid contained in the gases from zinc, lead, or copper furnaces, by allowing the gases to ascend towers, where they come in contact with a descending stream of sulphuric acid.

Winkler describes a series of experiments made at the Schneeberg ultramarine works with a view of destroying the furnace-gases, which contain large quantities of sulphurous acid. The latter has a most disastrous influence on the forests in the vicinity of these works. The experiments of passing the gases through coke scrubbers, over which water is constantly pouring, were not successful. The same result was obtained when the gases were introduced into lead-towers filled with coke, over which nitrous sulphuric acid is pouring. The next trial consisted in utilising the sulphide of sodium obtained in the lixiviation process. It was found that although the sulphurous acid was completely absorbed, and the sulphide of sodium (obtained from the sulphate) had disappeared, a separation of sulphur could not be effected. However, it was shown that at the ordinary temperature sulphurous acid forms with sulphide of sodium thiosulphate of sodium with separation of sulphur, but at 40° tetrathionate of sodium is exclusively obtained. A practical method based on this circumstance was worked for a number of years at the above works. However, the value of the recovered sulphur did not cover the working expenses, and the method was abandoned. In its place, limestone and water was used (*ibid.*, **235**, 220), and the sulphurous acid sacrificed.

Hasenclever passes the gases from the furnaces through lead towers, then through carbonate of calcium or caustic lime, in order to form acid sulphite of calcium, which is worked up into sulphur and thio-sulphates, in conjunction with sulphide of calcium or soda residues.

In order to collect the dust from lead furnaces, Lewis passes the fumes through a worm into a series of filter bags. D. B.

Hydrogen Peroxide. By A. H. MASON (*Chemist and Druggist*, 1881).—The author gives a *résumé* of the literature relating to the preparation, properties, detection, estimation, and applications of peroxide of hydrogen. He thinks Thomsen's method of preparation the best available at present: the crude barium peroxide, after having been purified by precipitation from its solution in hydrochloric acid by baryta-water, is exactly decomposed by dilute sulphuric acid.

Schöne's colorimetric method appears to be the most delicate for estimating small quantities of the peroxide: the blue colour produced by the liberated iodine, when potassium iodide and starch solution are added to the liquid to be tested, is compared with standard colorations properly graduated. The ordinary method of estimating the strength of strong solutions is by measuring the volume of oxygen they can

evolve; by a ten-volume solution is understood one which evolves ten times its volume of oxygen.

The therapeutical value of the peroxide seems to be small, judging by the quantity sold for medicinal purposes. But as a disinfectant it is largely used in dilute solution.

Hydrogen peroxide is, however, a valuable agent for bleaching hair, ivory, oil, wax, tobacco, and blood serum, and for cleaning old engravings and oil paintings: for these purposes its solution should be made strongly alkaline by addition of the strongest ammonia.

The use of the peroxide for the above purposes on the large scale is very much limited by its costly nature, and any cheap method of preparation would largely extend its sale. F. C.

Extraction of Potash from Suint of Russian Wool. By FLEKKEL (*Bull. Soc. Chim.* [2], 34, 332—333).—The wash-water yields on evaporation a black resinous mass, forming 20·33 per cent. of the wool. This on incineration yields a mixture of carbon and potassium carbonate containing potash = 43·44 per cent. of the resinous mass, or 8·81 per cent. of the wool. The potash, extracted by water, contains 85 per cent. pure K_2CO_3 , and is the purest commercial variety.

J. M. H. M.

Inflammation by Nitric Acid. By K. KRAUT (*Ber.*, 14, 301—302).—Regarding the disputed point whether nitric acid (sp. gr. 1·5—1·52) can inflame vegetable material, the author states that some seven years ago he investigated this matter, and found that straw, hay, cotton, saw-dust, and like materials can easily be inflamed by nitric acid. P. P. B.

Loss of Oxides of Nitrogen in the Manufacture of Sulphuric Acid, and a means of Preventing it. By LASNE and BENKER (*Compt. rend.*, 92, 191—194).—Even in the best conducted works using Gay-Lussac towers there is always a certain loss of oxides of nitrogen, necessitating a corresponding expenditure of sodium nitrate. The gases issuing from the chambers must contain at least 5 per cent. of oxygen, in order to ensure the complete oxidation of the sulphurous anhydride, and the only oxide of nitrogen which can exist in presence of this excess of oxygen is the tetroxide, yet the sulphuric acid which flows from the bottom of the tower contains only the trioxide. Nitrogen tetroxide dissolves in sulphuric acid of 62° B., and can under certain conditions combine with it, but the compound formed is very unstable, and its tension of dissociation is so great even at ordinary temperatures, that a current of air or of dry carbonic anhydride, or a slight elevation of temperature, is sufficient to expel the tetroxide. The gas which enters the bottom of the tower contains only about 0·3 per cent. of nitrogen tetroxide, its tension is consequently very feeble, and it is easy to understand that the sulphuric acid can only absorb a small proportion of it. Indeed no sensible trace of this gas can be detected in the acid which runs from the bottom of the tower. Nitrogen trioxide, on the other hand, forms a definite stable com-

pound, the so-called "chamber crystals," not destroyed by the passage of sulphurous anhydride, or by a moderate elevation of temperature, but decomposed by water.

The authors have observed that the quantity of nitrous acid in the sulphuric acid running from the Gay-Lussac tower is smaller the higher the proportion of oxides of nitrogen in the gases coming from the chambers, but that the loss of these oxides diminishes as the intensity of the colour of the gases which enters the tower decreases. In the latter case they have always been able to prove the presence of a small but variable quantity of sulphurous anhydride, the coexistence of which with nitrogen tetroxide can only be due to imperfect mixture of the gases. The gases, moreover, are almost, but not quite, dry. The sulphurous anhydride reduces the nitrogen tetroxide to trioxide, which at once combines with the sulphuric acid produced at the same time, forming the stable nitrosyl sulphate. The reaction takes place between two equivalents of each gas; 1 mol. of nitrogen trioxide is retained in the compound, the other is again oxidised, and again goes through the same reactions. The sulphuric acid falling over the coke in the tower simply serves to dissolve and remove the nitrosyl sulphate; it only acts chemically in the exceptional case in which it meets with nitrogen trioxide ready formed. The presence of a small quantity of moisture in the gases is essential, for if perfectly dry no reaction takes place; on the other hand, an excess of aqueous vapour would decompose the nitrosyl sulphate. In practice, it is impossible always to obtain the right proportion of nitrogen tetroxide and sulphurous anhydride in the gases issuing from the chambers: an excess of oxides of nitrogen is always employed, even at the risk of loss. The authors obtain the required proportion by injecting sulphurous anhydride in a proper state of humidity into the bottom of the tower, and in this way they have been able to reduce the expenditure of nitrate to one-third its original amount. When adopting this plan, a larger proportion of oxides of nitrogen may be employed, and the gases may be passed more rapidly through the chambers, thus rendering it possible to burn a greater quantity of pyrites for a given cubical space.

C. H. B.

Applications of Lead Chamber Crystals. By C. GIRARD and J. A. PABST (*Bull. Soc. Chim.* [2], **35**, 98—100).—The lead chamber crystals, consisting of nitrosyl sulphate, may be employed for deodorising the gases evolved in the manufacture of ammonium sulphate, in the drying of night soil, &c., by passing them through towers charged with coke, down which a solution of the crystals trickles. The gases should not contain more moisture than an ordinary saturated atmosphere, and should be brought to that state by cooling before entering the tower. The waste acids from the manufacture of gun-cotton and nitrobenzene may be used for this process.

Nitrosyl sulphate has many advantages over chloride of lime as a disinfectant, notably that the sulphuric acid left may be used in the manufacture of ammonium sulphate and superphosphate, whereas the residue from bleaching powder is practically useless.

L. T. O'S.

Bohemian Chalk Fossils. By J. STOKLASA (*Landw. Versuchs.-Stat.*, **25**, 291—299).—I. Coprolites. Two kinds were examined from whitish-grey beds near Teplitz. An elliptical spirally-shaped variety, of brownish colour, was found to give from 4 to 16 per cent. of phosphoric acid. The kernel consists mainly of calcium phosphate and carbonate, with sometimes a little iron phosphate. The external portion consists mainly of iron phosphate, sometimes with calcium phosphate, and calcium or aluminium silicate. In the second variety, of a pointed oval shape, the phosphoric acid seems to have been almost completely removed, calcium carbonate replacing the phosphate.

II. *Lepidendron longissimum* occurs in quantity in the Teplitz beds. It is a tube-shaped fossil of very variable composition, in which calcium, aluminium, and iron phosphates occur, along with carbonates.

III. Shark's teeth. Analysis shows the original calcium phosphate to have been changed into iron phosphate, which thus forms the chief constituent of the teeth. The amounts of potash, soda, and magnesia are very small, and the lime is only from two to six per cent.

J. T.

Clay and Earthenware Goods. (*Dingl. polyt. J.*, **239**, 210—215.)—Pabst has investigated Chinese and Japanese earths used in the manufacture of porcelain, which were brought to him by Richt-hofen on his return from China and Japan. The Chinese rocks are porcelain materials, which are worked up in King-te-tshönn—situated to the east of Pojang-hu, in the province of Kaing-si—a district where porcelain has been manufactured for thousands of years. These rocks resemble petrosilex in character. The following analyses represent the composition of rocks occurring near Ki-mön-hsiën:—

	No. 1.	No. 2.	No. 3.	No. 4.
SiO ₂	74·60	75·61	74·31	74·10
Al ₂ O ₃	16·46	15·60	16·39	16·28
CaO	2·58	0·75	1·60	0·73
K ₂ O	2·82	2·54	5·90	4·76
Na ₂ O	1·89	2·46	0·57	0·42
H ₂ O	2·42	2·72	2·41	3·42
	100·86	99·69	101·18	100·69

No. 2 is a stamped ore buddled from No. 1. No 4, ditto from 3. These rocks are entirely free from iron.

Another class of rocks found at Yü-Kan-hsien is used only at the royal porcelain factories. A mass of rock, which is now entirely exhausted, was situated at Kan-ling, near Tan-liang-hsien, from which the name "Kaolin" is said to have been derived. According to Richt-hofen these masses of rocks are said to be spread over the region of phyllite, hence the Chinese porcelain rocks about King-de-tshönn belong to the archaic formation.

With regard to the Japanese rocks occurring at the felspathic regions near Arita (province of Hinzen), specimens of early origin, perhaps of tertiary origin, have been found. Their amalgamation with perlite and rhyolite-breccia, found in the vicinity of the moun-

tain, as well as the presence of members of the trachyte and basalt groups in this volcanic district, affords proof of the fact that these porcelain rocks are connected in a certain degree with the eruption of these tertiary masses of rocks. The following is their composition:—

	SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	H ₂ O.
I. Porcelain material from Tsudzi-toutschi	78·27	14·69	0·44	4·23	2·99
II. Porcelain material from Jakai-ime-toutschi . .	77·88	14·78	0·33	3·55	2·84
III. Material for glazing (Uwa-k'suri)	77·05	15·28	0·40	3·98	2·91
				D. B.	

Resistance of Toughened Glass to Flexure. By DE LA BASTIE (*Compt. rend.*, **92**, 194).—From the results of a large number of experiments, it is found that the elasticity of toughened glass is more than double that of ordinary glass, and that toughened sheets bend much more readily than ordinary sheets. Single toughened glass has a resistance 2·5 times, and demi-double toughened glass a resistance 3·1 times, that of ordinary double glass. Polished toughened sheets, of thickness varying from 0·006 metre to 0·013 metre, have a resistance 3·67 times as great as that of ordinary sheets of the same thickness, and the resistance of rough toughened sheets is 5·33 times that of ordinary rough sheets.

C. H. B.

Condition of Carbon in Steel and the Effect of "Hardening" upon It. By T. W. HOGG (*Chem. News*, **42**, 130—132).—In connection with the observations published by Parker (*Chem. News*, **42**, 88), the author some time ago obtained a similar series of results, whilst trying a number of hardening experiments for some large iron works. The results, apart from the considerations to be applied to the various phenomena connected with hardening, point out the probable cause of the discrepancies which frequently occur amongst chemists, for it is evident that two samples of steel may yield identical results by colour-test, and yet differ very considerably by combustion. In fact, by hardening the samples at different temperatures, or cooling in different fluids, it seems possible to cause the sample to yield any required colour-test within certain limits.

From his results the author concludes that iron forms a definite compound with carbon at high temperatures, but this compound is very unstable and gradually decomposes when the material in which it exists is allowed to cool slowly: on the contrary, it is prevented from decomposing if the heat is suddenly abstracted; the more rapid the abstraction of heat, the more of this compound is left undecomposed, and the harder therefore will be the steel.

The theory which the author thinks is at present most favourably looked on as explaining the phenomena of "hardening," may be summed up as follows:—"The violent compression produced as a result of the sudden cooling, causes the carbon to combine or enter into a more intimate union with the iron." In opposition to this the author places the following as one tending to a more satisfactory

explanation:—"That the rapid abstraction of heat partially prevents the decomposition of an unknown unstable compound of iron and carbon, the presence of which compound communicates the peculiar properties of hardened steel." D. B.

On an Explosion Produced while Heating Wine, and a New Process for the Estimation of Alcohol. By V. WARTHA (*Compt. rend.* 90, 1008).—During the distillation of a quantity of Tokai, a violent explosion took place in the receiving cask. As the liquid which comes over has a temperature of about 40°, and is very rich in alcohol, it is supposed that the vapour given off from it spread to some neighbouring flame, and thus communicated with the interior of the cask.

The author has determined the minimum temperatures at which mixtures of alcohol and water take fire, with the following results:—

Alcohol per cent. . .	8	9	10	11	12	15
Lowest temperature of inflammation . .	55°	53°	51°	50°	48°	43°

The author hopes to found, upon these facts, a new method for the estimation of alcohol. C. W. W.

Oxygen and Alcoholic Fermentation. By A. MAYER (*Landw. Versuchs.-Stat.*, 25, 301—325).—C. v. Nägeli, in a publication *Die Gährung*, 1879, *München*, asserts the direct advantageous influence of oxygen on fermentation. Mayer examines the data on which this assertion is founded, viz., Pasteur's experiment, and some experiments made by W. Nägeli, and shows that Pasteur's experiments are insufficient. Five double experiments of W. Nägeli are discussed, in which sugar solutions, with the addition of yeast, are allowed to ferment in contact with air, with and without agitation; in some cases citric acid was added. To compare the results obtained, Mayer divides the weight of sugar fermented by the product of the time into the weight of yeast added, this gives "average fermentative power." The results show that usually more dry sugar is fermented per day (of 24 hours) than is equal in weight to the yeast added. In some cases less has been obtained, and this requires explanation. W. Nägeli has succeeded in showing the very favourable influence of the atmosphere on the apparent fermentative power of yeast whose power has been previously reduced to a small fraction by the addition of an organic acid; the less vigorous yeast cells being killed by the acid, afford food to those still living, whose increase is now favoured by the presence of oxygen. C. v. Nägeli asserts that there was no increase in the amount of yeast in W. Nägeli's experiments. This was inferred simply from the absence of suitable food; but Pasteur has shown that yeast increase can always be detected during the fermentation of sugar solutions where the yeast is less than 15 per cent. of the sugar. An increase of yeast must be admitted in W. Nägeli's experiments, in those cases where excess of oxygen was present, i.e., where the solution was agitated, and this would almost suffice to explain the increased fermentative power obtained. If the growth of

yeast is not sufficient to explain Nägeli's results, two other considerations must be dealt with before Nägeli's conclusion can be accepted. First, to ascertain if the fermentative power of growing yeast is greater than that of fully developed yeast. W. Nägeli used cane-sugar, which does not ferment until converted by means of a chemical ferment provided by the yeast: possibly the inversion would proceed more quickly in the solutions agitated, whilst in the others it would proceed by diffusion only.

Mayer examined the fermentation of cane-sugar, after inversion by means of sulphuric acid, under the action of yeast in atmospheres of air, nitrogen, and carbonic anhydride respectively; the fermentative powers thus obtained were 3·2, 3·1, and 3·4, respectively. The growth of yeast was greatest in air, less in nitrogen, and least in the carbonic anhydride, this result in the two latter cases being due to the fact that the nitrogen could not be so completely freed from oxygen as the carbonic anhydride. The fermentative power as given by the numbers above, if anything, is slightly diminished by the presence of oxygen in the air and the nitrogen. Confirmation of this view is afforded, firstly, because in the presence of oxygen the growth of yeast is greater; and, secondly, as he shows later, the fermentative power of young growing yeast is stronger than that of old and partly dead yeast. In the presence of air, we have a more active yeast; consequently the fermentative power of one and the same yeast has a higher value in the absence of air.

Three more experiments were made, in which potassium phosphate, magnesium sulphate, and calcium phosphate, were added to supply the ash constituents of yeast. The fermentative powers in the case of air, nitrogen, and carbonic anhydride, were now 3·16, 2·96, and 3·10 respectively; results very nearly identical, and very similar to those previously obtained. With air and nitrogen, most yeast was produced. These results indicate that if oxygen has any action on fermentation it is injurious.

When yeast extract was added to the vessels, similar results were obtained.

Mayer next mentions briefly the views of previous investigators.

J. T.

Recovery of Cane-sugar from Molasses by Fermentation.

By U. GAYON (*Bied. Centr.*, 1880, 835—838).—It is found that pure *Mucor circinelloides* ferment only attacks the directly fermentable sugars, or glucoses, not affecting the saccharoses, and moreover that it is a more powerful ferment than the ordinary beer ferment, but unlike yeast, it cannot produce fermentation unless there is a sufficient supply of nourishment for its propagation. These facts will be of great service to the sugar industries, in that the cane-sugar can now easily be obtained from the molasses as follows: the molasses should be diluted until the glucose is present to the amount of not more than 10 per cent., the glucose may then be fermented by means of *M. circ.*, which does not act on the saccharose, and the action is not retarded by even 30 per cent. of saccharose; the fermentation must be preceded by heating the molasses to boiling, and allowing it to cool in closed

vessels; the most advantageous temperature is 35—40°; care must be taken that only the *mucor ferment* is present, but it may be used repeatedly for several operations. E. W. P.

Tanning. By K. SADOW (*Dingler*, **239**, 68—71).—Putz has patented a mode of tanning skins, which consists in dissolving blood, fibrin, gluten, animal fibre, hairs, wool-refuse, horn, claws, feathers, &c., in soda-ley, mixing the concentrated solution with fat (5—10 per cent.), and precipitating the mixture with sulphate of aluminium. The skins having been treated with alum and salt, are tanned with the precipitate until completely saturated; they are then pressed strongly, oiled, dried, stretched, and curried. The tanning is said to be water-proof, and leather tanned in this manner possesses great softness and pliability. Eitner correctly calls this operation "alum-tanning," the albuminous precipitate with alumina injected into the skins serving merely as a "filling agent" to give the skins their requisite degree of fulness and a better cut, as mineral tannin is absorbed by the skins only in a limited measure.

The author discusses the difference between mineral leather and the so-called "oozed leather." The most important distinction between them is the behaviour of both when treated with pure water. Oozed leather does not alter its physical conditions when soaked in water; it maintains its firmness and pliability, while mineral leather loses its original character and assumes the properties which raw skins possess. Other differences of minor importance exist between these leathers, such as the changes exhibited in the drying process, the absorption of tannin by the skins, &c., all tending to show the superiority which oozed leather has over mineral leather.

King has patented a process of tanning skins, whereby the ordinary method is said to be facilitated very considerably. The author entertains some doubt as to the practicability of the process. Although he agrees in some measure with the active motion and the constant renewal of tannin, which appear to be the main features in the new process, he thinks that the great consumption of motive power and the constant and intimate contact of the tannin with the air, hinder the practical results which the method originally promised. D. B.

Celluloid. By F. BÖCKMANN (*Dingler*, **239**, 62—69).—Celluloid is prepared on a large scale either by treating pyroxylin with melted camphor or with an alcoholic solution of camphor, or by the action of a mixture of ethyl or methyl alcohol and camphor on pyroxylin. With regard to the properties of celluloid, the author has shown that neither heat nor percussion, blow nor friction would cause celluloid to explode. When brought into contact with a flame it burns like paper, and after the flame is extinguished it goes on smouldering, the camphor being distilled off with evolution of thick clouds of smoke, whilst the pyroxylin undergoes imperfect combustion. The percentage of ash varies between 1·31 and 2·18 per cent. in celluloids of different origin.

The sp. gr. varied very slightly in the various makes, from 1·3103 to 1·3926. By heating celluloid with ether, the whole of the camphor

is dissolved and can be separated from the pyroxylin and ash-constituents by filtration. When it is boiled with alcohol for several hours, the solution gradually assumes a syrupy consistency, and on the addition of water the dissolved pyroxylin separates in a gelatinous form. This when evaporated on a water-bath leaves a large residue of pyroxylin. Celluloid is completely soluble in ether-alcohol (excepting the ash constituents and colouring matters insoluble in this solvent). Wood-spirit behaves like ether. It is also soluble with ease in a concentrated boiling soda solution, and very rapidly soluble in warm nitric acid (2 vols. nitric acid to 1.5 vol. water). It is readily soluble in acetic acid and on adding water both camphor and pyroxylin are reprecipitated. Celluloid dissolves in a moderately dilute warm solution of sulphuric acid. Concentrated acid carbonises it. D. B.

Spontaneous Ignition of Coal. By H. HAEDICKE (*Dingl. polyt. J.*, **239**, 148—150).—Richter's experiments tend to show that the decomposition of coal in the presence of moisture depends on the pyrites, whilst the destructive action of oxygen occurs only at an elevated temperature, and is checked by the presence of moisture. The influence which pyrites may exercise on the decomposition of coal is of a twofold nature. It becomes first oxidised by the co-operation of moisture, and is transformed into ferrous sulphate; and during its formation the coal becomes split up and exposes a larger surface to the air; this ferrous salt is then oxidised into the ferric salt, which gives up oxygen to the coal.

These assumptions throw some light on the causes of spontaneous ignition, which are mainly attributable to the action of pyrites. The author found that pyrites ignites in pure oxygen at a temperature of about 200°. He attaches great importance to this subject, and gives some statistics as to the occurrence of accidents through spontaneous ignition—no less than 70 accidents were recorded among 31,116 ships in 1874 as resulting from this cause. To prevent spontaneous ignition, it is especially requisite to exclude all currents of air, unless the latter is passed through from the commencement in a strong current so as to act as a cooling agent. As moisture prevents ignition and accumulation of oxygen, it is desirable to introduce a jet of steam if there is any great increase of temperature in the coal.

D. B.

Solid Preparation of Bisulphide of Carbon for Vines. By J. LAFAURIE (*Compt. rend.*, **91**, 964).—The author prepares, for use against the phylloxera, a solid resulting from the intimate mixture at 35° or 40° of bisulphide of carbon with a solution of certain algæ, preferably of *Japan moss*. The amount of sulphide in the preparation may be as much as 80 per cent., and the evaporation is very slow, a large quantity of the bisulphide having been found in a piece that had been exposed to the air for two months. R. R.

Aqueous Shellac-varnish. By J. M. EDER (*Dingl. polyt. J.*, **237**, 466—467).—With well-sized paper a simple dilute borax shellac decoction is sufficient. With rough paper the following is excellent:—

300 parts water, 24 borax, 4 soda, 100 fresh bleached shellac, and about 10 dextrin; mix, boil down, and filter. Unfortunately the varnish has a yellowish tint. The addition of cochineal-red, &c., gives a pleasant tint.

Geissler remarks that bleached shellac becomes insoluble in borax solution after long exposure to the air. J. T.

New Dyestuff. (*Dingl. polyt. J.*, **237**, 464—466.)—Bindschedler and Busch prepare a green dye from tetramethyldiamidotriphenylmethane, by heating 100 parts with 500 parts sulphuric acid on a water-bath, until a test sample dissolves in alkaline water. The mass is thrown into water, neutralised with soda, then slightly acidified with acetic acid, and slowly decomposed with 75 parts lead peroxide suspended in cold water; after neutralising with soda and filtering, the sodium salt of the new dye comes down on evaporating; on treating with dilute hydrochloric acid, the new sulphonic acid is separated.

J. T.

Pigment for Floors, Wood, Stone and Brickwork. By F. MARECK (*Dingl. polyt. J.*, **239**, 401).—The following mixture produces a pigment which is used for "priming" instead of the more expensive oil colours and lakes. 60 grams of light-coloured joiner's glue are soaked over night in cold water and dissolved in a thick solution of milk of lime prepared from 500 grams caustic lime. The mixture is well agitated, boiled and treated with linseed oil until the latter no longer saponifies with the lime-glue (about 250 grams). The pigment produced on cooling can be mixed with any colour which is not altered by lime. When used for painting on wood, it is advisable to mix the pigment with one-fourth of its volume of a solution of shellac and borax, which must be prepared at the boiling heat. D. B.

Hops of Southern Europe. By TCHECH (*Bull. Soc. Chim.* [2], **34**, 346).—The wild hop of Styria, Croatia, Slavonia, Servia, and Bosnia, contains 5 to 8 per cent. tannin, that is, more than the common hop, and about one-third of the lupulin and essential oil of the latter. The author proposes its employment in mixture with the common hop for brewing beer. J. M. H. M.

Seeds of Cassia Occidentalis from Martinique. By J. MÖLLER and J. POHL (*Bied. Centr.*, 1880, 844).—The seeds of *Cassia occidentalis*, known also by the name "Mogdad coffee," are egg-shaped, 4.5 mm. long, 2.9—3.6 mm. broad, 1.2—1.59 mm. thick, and weigh 16 mgrms. apiece; the colour is grey-yellow, and the seed is coated with a white thin skin. The composition of the air-dried seed is in parts per 100:—Ash, 4.33; non-nitrogenous matter, 3.86; nitrogenous matter, 15.13; cellulose, 21.21; oil, 2.55; mucilage, 36.6; tannin acid, 5.23; water, 11.09. E. W. P.

Decomposition of Explosives in Closed Vessels; Composition of the Gases formed. By SARRAU and VIEILLE (*Compt. rend.*, **90**, 1058).—The following table gives the volume in litres, and composition of the gases formed per kilo. of substance exploded.

A, pure gun-cotton; B, gun-cotton with potassium nitrate; C, gun-cotton with ammonium nitrate; D, nitroglycerol; E, ordinary blasting powder.

	CO.	CO ₂ .	H.	N.	O.	C ₂ H ₄ .	H ₂ S.	Total volume in litres.
A ..	234	234	166	107	—	—	—	741
B ..	—	171	—	109	45	—	—	325
C ..	—	184	—	211	6	—	—	401
D ..	—	295	—	147	25	—	—	467
E ..	64	150	4	65	—	4	17	304

The gun-cotton was found by analysis to be a mixture of three parts trinitrocellulose with one part dinitrocellulose. It was found that the amounts of carbonic acid and hydrogen increased, and those of carbonic oxide and water decreased as the pressure of explosion was increased.

To render the combustion of gunpowder complete, ammonium nitrate was found superior to potassium nitrate.

In the explosion of nitroglycerol, the carbon and hydrogen are completely oxidised.

C. W. W.

General and Physical Chemistry.

A Simple Process of Slow Actinometry. By A. DOWNES (*Chem. News*, 42, 178).—In 1877-78 the author in conjunction with Blunt demonstrated the destructive action of sunlight on bacteria and other low organisms, and adduced evidence to show that this was due to excessive oxidation, under insolation, of their protoplasmic substance. In the course of this investigation, it was found that a decinormal solution of oxalic acid was, after a certain interval, entirely decomposed in sunlight by oxidation, thus:— $2\text{C}_2\text{O}_4\text{H}_2 + 2\text{O}_2 = 4\text{CO}_2 + 2\text{H}_2\text{O} + \text{O}_2$; the view taken in the above formula being that in sunlight the affinity of oxygen for the basylous hydrogen is so stimulated as to exceed that of the chlorous radicle C_2O_4 , just as, under other circumstances, oxygen itself may be superseded by chlorine. In darkness the balance is not disturbed, and ordinary oxygen has no power to displace the oxalyl radicle. Solutions of oxalic acid may be preserved for long periods if the light be carefully excluded and care taken to prevent decomposition by fungi. In connection with an investigation for the purpose of expressing arithmetically the oxidising power of sunlight during intervals of days, weeks, or months, it occurred to the author to turn this oxalic acid reaction to account. A measured quantity of decinormal oxalic acid is exposed in small-sized test-tubes, and after the desired period of insolation the amount of oxidation is determined by direct titration with potassium permanganate. In this way, weekly observations have been made since last March, and rough as these are, the results lead the author to believe that this process may become one of great value to the meteorologist, agriculturist, and sanitarian.

D. B.

Photographic Spectra of Stars. By W. HUGGINS (*Sill. Jour.* [3], 19, 373; *Nature*, January 22nd, 1880).—Photographs have been obtained of thirteen stars, three planets, and of different small areas of the moon. The spectra of Sirius, Vega, α Cygni, η Ursæ Majoris, α Virginis, α Aquilæ, and Arcturus, have been laid down on the scale of Cornu's map of the ultra-violet part of the solar spectrum; they extend from about G to O.

Six of these spectra belong to stars of the white class. The photographs present a remarkable typical spectrum consisting of twelve strong lines, the least refrangible of which is coincident with the hydrogen line γ near G, the second with h , and the third with H; K is generally absent; if present, it is thin and inconspicuous.

These lines H and K are generally attributed to calcium, but there is another pair of strong lines in the calcium spectrum (wave-length = 3736.5 and 3705.6), and these lines never appear in the spectra of white stars.

The twelve lines found in the spectra form a group in which the distance between any two adjacent lines is less as the refrangibility increases. These lines are probably due to one substance, and two at least belong to hydrogen.

The photographed spectra of the planets Venus, Mars, and Jupiter show no sensible modification of the violet and ultra-violet parts of the solar spectrum.

Numerous spectra of small areas of the moon's surface have been taken under varying circumstances. The results are wholly negative as to any absorptive action of a lunar atmosphere. C. W. W.

Absorption Spectra of Cobalt Salts. By W. J. RUSSELL (*Chem. News*, 43, 27—28).—Anhydrous cobalt chloride obtained by different methods always gives the same spectrum. The bromide gives a similar spectrum, but the bands are less refrangible. When cobalt chloride is fused with potassium, sodium, or zinc chlorides, a green mass is obtained which gives a spectrum different from that of cobalt chloride alone. The same spectrum is given by solutions of the chloride in hydrochloric acid, ethyl and amyl alcohols, ethereal salts, glycerol, or any menstruum in which it dissolves freely without definite combination. In these experiments care was taken to exclude any traces of moisture. Under similar conditions, the bromide and iodide give spectra corresponding with those of the chloride, but the bands of the iodide are less refrangible than those of the bromide, and those of the bromide than those of the chloride. Since cobalt chloride gives the same spectrum when fused with other metallic chlorides as when dissolved in the liquids mentioned, this spectrum must be due to the anhydrous chloride in a molecular condition different from that in which it exists when fused alone.

The spectrum of the hydrochloric acid solution of cobalt chloride is a test of extreme delicacy, is remarkably persistent under varying conditions, and is the same whatever the strength of the solution. On the other hand, the spectrum of a solution in anhydrous alcohol containing only 20 grams in 100 c.c. is somewhat different from that of a nearly saturated solution; a new band is visible, and some of the old bands have disappeared. If the solution contains only about 0.008 gram of the salt in 100 c.c. it gives a totally different spectrum, but further dilution produces no change. Other liquids exhibit similar phenomena, but when the chloride is but slightly soluble, as in ether, only the first, or most dilute stage, is observed; if somewhat more soluble, as in glacial acetic acid, the first and second stages can be distinguished. When the finely powdered dry chloride is shaken up with a liquid in which it is insoluble, it gives a spectrum similar to that of the fused chloride.

Aqueous solutions of cobalt chloride containing between 25 grams and 0.1 gram in 100 c.c., give a broad absorption-band shading off on both sides, and the result is the same with both a long column of a dilute solution, and a short column of a strong solution. A saturated solution, however, gives a spectrum identical with that obtained by fusing cobalt chloride with potassium chloride, or by dissolving it in alcohol, &c. The action of heat and of bodies capable of combining with water, on aqueous solutions of the chloride is identical; both tend to destroy the absorption-band of the hydrate, and produce the spectrum of the anhydrous chloride.

The characteristic spectrum of cobalt oxide is well shown by the

precipitate formed when potash, soda, or ammonia is added to a solution of a cobalt salt. It is, as Vogel has pointed out, identical with that of cobalt glass. The spectra of the glass, and of the oxide precipitated by potash or soda contain a band not visible in the spectrum of the oxide precipitated by ammonia, and probably due to a compound of cobalt with the alkali. If the oxide is precipitated in presence of excess of cobalt salt, or if the precipitate is shaken up or warmed with a solution of cobalt chloride, an oxychloride is formed which gives a definite spectrum. The decomposition of this compound by water may be traced by corresponding changes in its spectrum. It would appear that the blue precipitated oxide is not a hydrate, although very liable to change.

Aqueous solutions of the iodide and bromide behave with alkalis in a manner similar to the chloride, but the bands are less refrangible the greater the molecular weight. Aqueous solutions of cobalt salts of the oxyacids give absorption-bands standing off like those of the hydrate, and not sharp bands like those of the haloid salts. The oxide found in the precipitate formed by alkaline carbonates in solutions of cobalt salts, is the result of an after decomposition, and is not present in the precipitate when first formed. Cobalt phosphate dissolved in fused microcosmic salt gives, when cold, an indistinct banded spectrum of the phosphate. On heating, this spectrum disappears, and that of the oxide becomes visible: on again cooling, the spectrum of the phosphate reappears. Drawings of all the spectra accompany the original paper.

C. H. B.

Influence of the Molecular Grouping in Organic Bodies on their Absorption in the Infra-red Region of the Spectrum. By Captain W. DE W. ABNEY and Lieut.-Colonel FESTING (*Chem. News*, 43, 75).—The authors describe the apparatus used by them in their research and their plan of mapping the absorption-spectra, the results being given in wave-lengths. The source of light for obtaining a continuous spectrum was the incandescent positive pole of an electric light, the electricity being generated by a Gramme machine. The light was passed through tubes containing the fluids, and the absorption-spectra photographed in the infra-red region. The absorptions are classed as follows:—

1st. General absorption at the least refrangible end of the spectrum.

Lines $\left\{ \begin{array}{l} \text{Fuzzy.} \\ \text{Sharp.} \end{array} \right.$

Bands . . $\left\{ \begin{array}{l} \text{Both edges sharply defined.} \\ \text{One edge sharply defined.} \\ \text{Both edges less sharply defined.} \end{array} \right.$

The authors next discuss the causes of the different absorptions met with in various fluids. They find that the presence of lines is due to the hydrogen in the bodies, and show that the termination of the bands in liquids containing carbon, hydrogen, and oxygen, corresponds with the position of these hydrogen lines. It therefore appears to them that the bands are in reality a blocking out of radiation between two hydrogen lines. They then point out that each radical has its

own definite absorption in the infra-red, and that such a radical can be detected in a more complex body.

The paper closes with an appendix giving tables of the bands and lines found in a large number of substances, of which also there are maps. D. B.

Displacement of the Absorption-bands of Purpurin in Alum Solutions. By H. MORTON (*Chem. News*, **42**, 207).—It was found that the position of the two principal absorption-bands of purpurin dissolved in alum solution was notably affected by the amount of alum in the solution. Thus a solution containing 2 per cent. of the salt showed the bands at conspicuously lower points than a solution containing 1 per cent., and this again showed a lower position than a solution containing $\frac{1}{2}$ per cent. The change seems to be gradual, and to amount to a depression of the bands by addition of alum to the solution, everything else remaining the same. A similar depression was found to be caused by heating these solutions, the band returning as they cooled. The displacement was towards the red end of the spectrum. In two cases the observations were: $50^{\circ} 26'$ and $50^{\circ} 27'$ when cold, and $50^{\circ} 20'$ and $50^{\circ} 21'$ when hot. The heat employed in the experiments did not destroy the purpurin. D. B.

Phosphorescence of Organic and Organised Bodies. By B. RADZISZEWSKI (*Annalen*, **203**, 305—336).—Compare Pflüger (*Archiv. gesam. Physiol.*, **10**, 275), Schultz (*Archiv. mikroskop. Anat.*, **1**, 125), Phipson (*Compt. rend.*, **51**, 51, 641; **75**, 547), Pauceri (*Ann. Sc. Nat.*, 5th Series), Pelletier (*Journ. Pharm.*, **7**, 579), Calloud (*Répert. Pharm.*, **16**, 177), Dessaignes (*Journ. Phys.*, **68**, **69**, **73**, **74**), E. Becquerel (*La Lumière*, **1**, 48 and 409), Radziszewski (*Ber.*, **10**, 70), Berthelot (*Bull. Soc. Chim.*, 1867, 109), Fudakowski (*Ber.*, **6**, 106), Quatrefages (*Compt. rend.*, **31**, 618), Biot and Becquerel (*Des forces physico-chimiques et leur intervention dans la productions des phénomènes naturels*, Paris, 1875, 83), Fabre (*Compt. rend.*, **41**, 1245), Gmelin (*Handbuch*, **1**, 170, 5th Edition), Della Valle (*La luce negli animali*, Napoli, 1875), Secchi (*Compt. rend.*, **75**, 321).

The author concludes from a number of experiments, for which reference must be made to the original paper, that *those organic compounds phosphoresce which in the presence of an alkali enter into chemical combination with active oxygen*. Such bodies are many aldehydes, grape-sugar, aldehyde-ammonias, hydrobenzamide, lophine, hydroanisamide, anisidine, furfurine, hydrocuminamide, terpenes, aromatic hydrocarbons, fatty compounds, and fatty oils (such as oleic acid, elaïdin, castor oil, &c.), alcohols of the paraffin series which contain more than four carbon-atoms, &c. In the case of the terpenes and many other bodies, the presence of active oxygen in the liquid may be attained by exposure to air and direct sunlight, the presence of such active oxygen being detected by the substance bleaching indigo. A gentle heat is required in most cases, but in some few the phosphorescence may be observed at the ordinary temperature; agitation of the liquid is also favourable to the production of the phenomenon. After a time it disappears, owing to all the active oxygen being used

up, but may be restored by exposure to air and sunlight. As active oxygen is produced during slow oxidation, it follows that slow oxidation is the most favourable condition for phosphorescent phenomena. It is true that active oxygen is also produced during violent oxidations, but in that case we term the phenomenon combustion. In general the act of combination of free oxygen-atoms with the constituents of a combustible body causes such an elevation of temperature that light is produced, and according as this light occurs in a comparatively few isolated points, or in very numerous points, we have phosphorescence or combustion. From this it follows that phosphorescence is merely a special case of ordinary combustion. That the presence of an alkali is most suitable for the exhibition of phosphorescence in carbon compounds is because it favours the formation of active oxygen, and also because it is very probable that more heat is evolved by the combination of oxygen with carbon in the presence of an alkali than in that of an acid. The phosphorescence of organised bodies and living animals is also due to slow oxidation taking place in presence of an alkali; for the author finds that many compounds which occur in the living organism, such as lecithin, fats, chlorésterin, spermaceti, wax, ethereal oils, &c., exhibit phosphorescent properties in the presence of such alkalis (choline, neurine, those of the general formula $(NR_4)OH$, &c.) as are found in organised bodies, and that very minute quantities are capable of producing this result. T. C.

Colours of Thin Blowpipe Deposits. By C. H. KOYL (*Sill. Jour.* [3], 20, 187).—The peculiar colours of the exterior rings of blowpipe deposits are due not to impurities, but to the fine division of the particles, resulting in the almost complete polarisation of the reflected light. C. W. W.

Chemical Constitution of Organic Compounds in Relation to their Refractive Power and Density. By J. W. BRÜHL (*Annalen*, 203, 255—285, 363—368).—This paper has appeared in an abridged form in the *Berichte* (13, 1520), the abstract of which will be found in this volume, p. 15. T. C.

Absorption of the Sun's Rays by the Carbonic Anhydride of the Atmosphere. By E. LECHER (*Ann. Phys. Chem.* [2], 12, 466—473).—The author concludes from his experiments that the absorption of the sun's rays usually ascribed to aqueous vapour is due rather to the carbonic anhydride present in the atmosphere, and founds thereon a method for determining the amount of that gas present in the air. T. C.

Some Remarkable Phenomena with Flames. By W. HOLTZ (*Ann. Phys. Chem.* [2], 12, 572—590).—These phenomena were observed with two gas-jets with fine openings, and burning without previous admixture with air. The orifices of the jets are about 0·8 mm. diameter, and the slim pointed flames about 90 mm. high. The flames completely coalesce when the burners are brought so close that the flames are in contact at their base and slightly inclined. After separating and inclining them so that they impinge directly on one

another, they coalesce only when the apex of the one strikes the base of the other, whilst in any other position the luminous parts are mutually repulsive, and always remaining separated by a fine but sharply defined dark space.

By allowing the flames to impinge at different angles, various forms of flame are obtained, some of which are silent, whilst others emit high or low notes. At a certain angle of inclination, and at a certain distance of the orifices, there appears at the lower periphery of the obliquely directed flame-disc, a red-hot glowing tube of carbon particles endowed with a spiral motion. T. C.

The Strict Meaning of "Galvanic Polarisation." By W. BEETZ (*Ann. Phys. Chem.* [2], **12**, 474—477).

Electromotive Power of Galvanic Combinations, consisting of Zinc, Sulphuric Acid, and Platinum, with Copper, Gold, and Carbon. By C. FROMME (*Ann. Phys. Chem.* [2], **12**, 399—425). —Exner (*Wien. Ber.*, **80**, 1055; *Wien. Ann.*, **10**, 265) has advanced the theory that polarisation is due solely to the recombination of the separated "ions," and that in the case of those elements which consist of the above combinations, a real polarisation cannot exist, because a recombination of the hydrogen with the oxygen which has entered into combination with the zinc is impossible. It is solely the convective action of the oxygen of the air dissolved in the liquid which causes the electromotive power of such an element to be greater at first than afterwards. So that if the liquid be previously freed from oxygen the electromotive power at once assumes a constant minimum value, which is independent of the strength of the current, and is equal for all the above combinations.

The author, however, cannot confirm this, for he finds that the electromotive power of those combinations is not the same, but different, and that for each combination the value is constant and independent of the amount of previously dissolved oxygen.

The question as to the maximum of hydrogen polarisation is still an open one, but this maximum is higher than is usually assumed. The measurement of the polarisation either with a closed current or shortly after opening does not give concordant results, owing to the rapid disappearance of the polarisation, and in order to obtain the real maximum value, it is absolutely necessary that it should be determined whilst the polarisation current lasts.

As regards the influence of concentration, the smallest addition of sulphuric acid to the water surrounding the platinum, gold, silver, or copper plate alters considerably the electromotive power, producing an increase in the case of platinum and gold, and a decrease in that of silver and copper. With gold and platinum, it attains a maximum with extremely dilute sulphuric acid, at which it remains for some time on the further addition of acid, then sinks to a minimum, and afterwards increases considerably, and finally slightly diminishes with very great concentration. For copper and silver, the electromotive power at first diminishes rapidly, and with silver continues to do so even with the most concentrated acid, whilst with copper a mini-

imum is attained, after which it continues to rise. The influence of the concentration of the nitric acid on the electromotive power of a Grove's element was also determined, and it was found to increase with the concentration, rapidly at first, and afterwards more slowly. This also holds good if the platinum plate is replaced by one of gold.

T. C.

Differences of Electric Tension between Liquids in Contact, with Special Reference to the State of Concentration. By E. KITTLER (*Ann. Phys. Chem.* [2], **12**, 572—590).—Compare Fechner (*Pogg. Ann.*, **48**, 1, 225); Wild (*ibid.*, **103**, 353); Schmidt (*ibid.*, **109**, 106); Bois-Reymond (*Reichert's und Bois-Reymond Archiv*, 458, 1867); and Worm-Müller (*Pogg. Ann.*, **140**, 114, 380).

From his experiments, the author draws the following conclusions: (1.) That aqueous solutions of the chlorides of ammonium, potassium, sodium, and nickel, obey Volta's law of tension, and that, irrespective of their state of concentration. This also holds good for the same chlorides in contact with distilled water, or with an aqueous solution of copper sulphate, and for various solutions of zinc sulphate in contact with water, and for solutions of zinc and copper sulphates; whereas solutions of the chlorides of ammonium, potassium, sodium, and nickel in contact with dilute acids, sulphuric and hydrochloric, do not obey the law. (2.) In the case of two solutions of the same chloride, the current in the liquid passes from the more to the less concentrated solution; and if one of these solutions is replaced by distilled water or a solution of copper sulphate, the current passes from the chloride to the water or copper sulphate, and this holds good whether the electrodes be silver, copper, or zinc. The direction which the current takes in several other combinations is also given.

T. C.

The Mechanical Equivalent of Heat. By H. A. ROWLAND (*Landw. Versuchs.-Stat.*, **26**, 324; and *Supp., Ann. der Physik*, 1880, 713).—The author has made a new determination of the mechanical equivalent, taking into account the change in the specific heat of water at different temperatures, and referring temperatures to an air thermometer. The numbers obtained for the same temperature differed very slightly from each other. The most probable value (A) is given in kilogram-meters for 1° at the latitude of Baltimore, and the temperature *t* of Thomson's absolute scale (for Paris add — 0·4, for Manchester and Berlin — 0·5.)

<i>t.</i>	A.	<i>t.</i>	A.	<i>t.</i>	A.	<i>t.</i>	A.
6	429·5	13	427·9	20	426·4	27	425·6
7	429·3	14	427·7	21	426·2	28	425·6
8	429·0	15	427·4	22	426·1	29	425·5
9	428·8	16	427·2	23	426·0	30	425·6
10	428·5	17	427·0	24	425·9	31	425·6
11	428·3	18	426·8	25	425·8	32	425·6
12	428·1	19	426·6	26	425·7	33	425·6

J. T.

Thermochemical Researches on the Sulphides. By SABATIER (*Ann. Phys. Chem.* [5], 22, 598).—The author has made a complete thermochemical investigation of the anhydrous sulphides of the metals of the alkaline earths, earths and alkalis, and of their combinations with water and sulphuretted hydrogen. The heats of formation and of solution of the alkaline polysulphides and hydrogen persulphide are also investigated.

Heats of Formation of Anhydrous Sulphide (S solid, H₂S gas).

Sulphide.	Molecular weight.	Heat disengaged.
K ₂ + S	110	+ 104.2—102.6 cal.
Na ₂ + S	78	+ 88.2 "
Ca + S	72	+ 92.0 "
Sr + S	119.6	+ 99.2 "
Mg + S	56	+ 79.6 "
Si + S ₂	92	+ 40.0 "
Al ₂ + S ₃	152	+ 124.4 "
K ₂ + H ₂ S + S	144	+ 128.0 "
Na ₂ + H ₂ S + S	112	+ 111.4 "
K ₂ + S ₄	206	+ 116.6 "
Na ₂ + S ₄	174	+ 98.4 "
(NH ₃) ₂ + H ₂ S + S ₃	164	+ 40.0 "
(NH ₃) ₃ + H ₂ S + S ₄	196	+ 40.4 "
(NH ₃) ₂ + H ₂ S + S ₇	324	+ 40.6 "
H ₂ S + Sn	34 + 32n	— 5.3 "
K ₂ S + H ₂ S	144	+ 19 — + 20.8 "
Na ₂ S + H ₂ S	112	+ 18.6 "
K ₂ S + S ₃	206	+ 12.4 "
Na ₂ S + S ₃	174	+ 10.2 "

Heat of Solution (10—17°).

K ₂ S	110	+ 8.2 — + 10 "
K ₂ S ₂ H ₂ O	146	+ 3.8 "
K ₂ S.5H ₂ O	200	— 5.2 "
Na ₂ S	78	+ 15.0 "
Na ₂ S.4.5H ₂ O	159	— 5.0 "
Na ₂ S.5H ₂ O	166	— 6.6 "
Na ₂ S.9H ₂ O	240	— 16.72 "
CaS	72	+ 6.10 "
SrS	119.6	+ 6.8 "
Bas	169	+ 7.0 "
K ₂ S.H ₂ S	144	+ 1.54 "
K ₂ S.H ₂ S $\frac{1}{2}$ H ₂ O	153	+ 1.24 "
Na ₂ S.H ₂ S	112	+ 8.8 "
Na ₂ SH ₂ S ₄ H ₂ O	184	— 3.0 "
K ₂ S ₄	206	+ 1.2 "
K ₂ S ₄ $\frac{3}{2}$ H ₂ O	215	+ 2.24 "
K ₂ S ₄ 2H ₂ O	242	— 7.5 "
Na ₂ S ₄	174	+ 9.8 "
(NH ₄) ₂ S ₄	164	— 8.2 "

Heats of Hydration.

Equation.	Solid water. Heat evolved.	For each mol. H ₂ O.
Na ₂ S anhydride + 4.5H ₂ O = Na ₂ S4.5H ₂ O ..	+ 13.6	3.08
Na ₂ S „ + 5H ₂ O = Na ₂ S5H ₂ O....	+ 14.46	2.88
Na ₂ S „ + 9H ₂ O = Na ₂ S9H ₂ O....	+ 18.86	2.08
K ₂ S2H ₂ O + 3H ₂ O = K ₂ S5H ₂ O.....	+ 4.6	
Na ₂ S.H ₂ S + 4H ₂ O = Na ₂ SH ₂ S.4H ₂ O	+ 6.14	
K ₂ S.H ₂ O + $\frac{1}{2}$ H ₂ O = K ₂ S.H ₂ S $\frac{1}{2}$ H ₂ O	- 0.42	
K ₂ S ₄ + $\frac{1}{2}$ H ₂ O = K ₂ S ₄ $\frac{1}{2}$ H ₂ O	+ 2.66	5.32
K ₂ S ₄ + 2H ₂ O = K ₂ S ₄ 2H ₂ O	+ 5.76	2.88

These numbers illustrate the general law that the loss of energy resulting from the fixation of 1 mol. of water, decreases rapidly with each successive hydrate.

Heat of Formation of Sulphides from the Base and Hydrogen Sulphide.

Equation.	Heat disengaged (H ₂ O gas).
CaO anhydride + H ₂ S gas = CaS anhydride + H ₂ O gas	13.6 cal.
SrO „ + „ = SrS „ „	21.6 „
BaO „ + „ = BaS „ „	22.10 „
Na ₂ O.H ₂ O sol. + „ = Na ₂ S.H ₂ S + 2H ₂ O gas ..	16.30 „
K ₂ O.H ₂ O „ + „ = „ + „ ..	28.96 „

These results compared with those above show that in the formation, whether by the direct combination of their elements, or by the action of sulphuretted hydrogen on the base, more heat is evolved in the potassium than in the sodium compounds.

Heats of Oxidation of the Sulphides.

Equation.	Heat disengaged.
CaS + O ₄ = CaO.SO ₃	+ 227.0
SrS + O ₄ = SrO.SO ₃	+ 230.6
BaS + O ₄ = BaO.SO ₃	+ 236.5

Several chemical points are also noticed by the author in the course of the investigation.

Alkaline Earth Sulphides.—It is found that the sulphides of the alkaline earths are best prepared by acting on the carbonates at a red heat with sulphuretted hydrogen; the sulphide obtained is then heated and allowed to cool in a current of hydrogen, in order to free the product from the last traces of polysulphides. The method proposed by Schöne of decomposing the carbonates with carbon bisulphide, does not yield satisfactory results.

Sulphides of the Alkalis.—The author endeavoured to prepare anhydrous sodium sulphide by a rapid dehydration of the hydrate Na₂S.9H₂O, but the product obtained contained polysulphides and silica due to the action of the polysulphides on the glass. The commercial hydrate, Na₂S.9H₂O, is never pure, it always contains carbonate

and thiosulphate; to free it from the latter, it must be dissolved in the smallest quantity of warm water, and the solution evaporated in a vacuum. Sodium hydrosulphide is prepared by the evaporation of a solution of the hydrated sulphide saturated with sulphuretted hydrogen; and anhydrous potassium hydrosulphide by dehydrating the crystalline hydrated salt in a current of dry sulphuretted hydrogen.

Polysulphides of the Alkali-metals.—An anhydrous polysulphide of potassium was prepared by the action of carbon bisulphide on red-hot potassium sulphate, but the product was not perfectly homogeneous, having a composition intermediate between the K_2S_6 of Berzelius and the K_2S_7 of Schöne. A purer substance can be obtained by the dehydration by dry hydrogen of the hydrate $K_2S_{4\frac{1}{2}}H_2O$; the same method was used for the preparation of the corresponding sodium compound. From a thermochemical study of the polysulphides, the author concludes that in dilute solutions each successive equivalent of sulphur dissolves with an evolution of the same quantity of heat: hence each polysulphide must be considered as a mixture of monosulphide and polysulphide in variable proportion. The author has confirmed Fritzsche's researches on the ammonium polysulphides (*J. pr. Chem.*, **24**, 460, and **32**, 313).

Silicon Sulphide.—In the preparation of silicon sulphide by heating amorphous silicon in a current of sulphuretted hydrogen, the author observed in the cold parts of a tube a large quantity of a yellowish-brown substance, consisting of a mixture of the ordinary sulphide, SiS_2 , and silicon. The author explains its production and the transference of the silicon, by supposing the formation of a volatile subsulphide at a low temperature, which at a higher temperature is decomposed into the subsulphide and silicon, the change being analogous to that of silicon sesquichloride. Other points have already been noticed in former abstracts (this Journal, 1879, 865, 866; 1880, 523, 689—691).

V. H. V.

Molecular Heat and Volume of the Rare Earths and their Sulphates. By L. F. NILSON and O. PETTERSSON (*Chem. News*, **42**, 119).—The rare earths, with a few exceptions (CeO_2 , ThO_2 , ZrO_2), belong to a group of sesquioxides. The specific densities and molecular volumes tabulated by the authors were obtained by means of a method specially adapted to prevent the errors arising from adhesion of air to pulverulent substances. The densities are therefore a little higher, and the molecular volumes slightly lower than the numbers usually given by others. The specific heats of the different compounds were determined by Bunsen's ice-calorimeter: the molecular weight of the different oxides was determined by a special analysis or synthesis of the sulphates, and the very same chemically pure substances were employed both for the thermic, volumetric, and magnetic experiments.

It is mentioned that hitherto it has been supposed that the atomic heat of oxygen in any oxide is not less than 3.5, or greater than 5.1. The numbers obtained by the authors, however, compel them to assign a still lower value to the atomic heat of oxygen in alumina and glucina, viz., 2.34. It enters into these oxides with a minimum capacity of heat and volume. From these earths upwards, the molecular heat

and volume of the sesquioxides gradually increase with increasing molecular weights. It is shown that the molecular heat of Er_2O_3 , Yb_2O_3 , La_2O_3 , and Di_2O_3 , nearly agrees with those for other sesquioxides determined by Regnault; that of G_2O_3 approaches to the same for alumina, and that of ZrO_2 , CeO_2 , and ThO_2 is as high as the values for SnO_2 , TiO_2 , and zircon determined by the same author, and for MnO_2 , according to Kopp. The validity of Neumann's law receives hereby a new confirmation. The molecular heat of the anhydrous sulphates of the sesquioxides varies only within very narrow limits; 61.60 to 68.96 for yttrium and didymium sulphate. The values for the salts of chromium, iron, indium, lanthanum, cerium, and didymium, are nearly identical, whilst even the values of glucinum, aluminium, scandium, gallium, yttrium, erbium, terbium, and thorium, approach each other very nearly.

Referring to their detailed paper on glucinum (*On the Essential Properties and Chemical Character of Glucinum*) the authors mention that this metal belongs on account of its sulphate— $3\text{K}_2\text{SO}_4 + \text{G}_2(\text{SO}_4)_3$ —to the series of the gadolinite and cerite metals, this salt having a composition typical for all the members of this series (G, Sc, Y, La, Ce, Di, Tr, $\text{Y}\alpha$, $\text{Y}\beta$, X, Er, Tm, Yb). The series of these elements, the leading member of which glucinum unquestionably is, stands certainly in the nearest proximity to another series, that of aluminium (Al_2 , Ga_2 , Tn_2 , Cr_2 , Mu_2 , Fe_2), but this nevertheless decidedly differs from the former by another typical double sulphate— $\text{K}_2\text{SO}_4 + \text{R}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ —or alum.

The following table shows the magnetic properties of the rare earths:—

Magnetic.	Diamagnetic.	
Cr_2O_3	G_2O_3	
Fe_2O_3	Al_2O_3	
Y_2O_3	Sn_2O_3	
Di_2O_3	Sc_2O_3 (?)	
Er_2O_3	La_2O_3	
Yb_2O_3	—	
—	ZrO_2	
CeO_2	ThO_2	D. B.

Benzene and Dipropargyl. By J. THOMSEN (*J. pr. Chem.* [2], **23**, 157—163).—A confirmation of the theory of the heat of formation of hydrocarbons in which the author maintains that the six carbon-atoms in benzene are united not by double bonds, but by nine single bonds.

Coefficients of Expansion of Lead Iodide and of Silver-lead Iodide. By G. F. RODWELL (*Chem. News*, **43**, 169).—The coefficients of cubical expansion for 1°C . of lead iodide, PbI_2 , are:—

Between 0° and 205°	0.00008317
„ 205° „ 253°	0.006378
„ 253° „ m. p.	0.000180

Silver-lead iodide, PbI_2AgI , containing—

PbI_2	66.206
AgI	33.794

between 0° and 118° has the cubical coefficient of 0.0000306. Between 118° and 124° it absorbs heat without expanding, and between 124° and 139° it contracts; at the last temperature it again absorbs heat without change of volume up to 144° , when it expands with a coefficient 0.0001150. The alloy has the same density at 0° , 130° , and 282° . It is probably owing to the presence of the silver iodide that like it and the chlorobromiodides of silver (*Proc. Roy. Soc.*, **25**, 292) it contracts during heating. This contraction, however, in the case of the alloy, begins 18° lower and ceases 6.5° lower than with silver iodide. The melting point of the alloy is 125° lower than that of AgI, and 19° higher than that of PbI_2 .

If the lowering of the melting point is due to the fact that similar particles of matter attract each other more strongly than dissimilar, and hence when the particles of two bodies are mutually diffused the contraction is less, and consequently the molecular motion is more readily assimilated. The same cause may serve to explain that the contraction begins 18° lower in the alloy than in silver iodide.

Silver chlorobromiodide, although containing 8 per cent. more silver iodide than the above alloy, contracts 20 times less than the latter, notwithstanding that the contraction in both cases must be traced to the same source.

L. T. O'S.

Specific Gravity and Volume-constitution of Formates. By H. SCHRÖDER (*Ber.*, **14**, 21—27).—The numerical results of the author's examination of formates are given in the following table, to which are appended the specific gravities and molecular volumes of formic and acetic acids, as determined by Pettersson :—

	Sp. gr.	Molecular volume.
$\text{CHLiO}_2 \cdot \text{H}_2\text{O}$	1.435	48.8
CHNaO_2	1.919	35.4
CHKO_2	1.908	44.0
$\text{CH}(\text{NH}_4)\text{O}_2$	1.266	49.8
$\text{C}_2\text{H}_2\text{BaO}_4$	3.212	70.7
$\text{C}_2\text{H}_2\text{SrO}_4 \cdot \text{H}_4\text{O}_2$	2.250	94.9
$\text{C}_2\text{H}_2\text{SrO}_4$	2.667	66.6
$\text{C}_2\text{H}_2\text{CaO}_4$	2.015	64.5
$\text{C}_2\text{H}_2\text{PbO}_4$	4.571	65.0
$\text{C}_2\text{H}_2\text{CdO}_4 \cdot \text{H}_4\text{O}_2$	2.441	97.5
$\text{C}_2\text{H}_2\text{MnO}_4 \cdot \text{H}_4\text{O}_2$	1.953	92.7
$\text{C}_2\text{H}_2\text{MnO}_4$	2.205	65.8
$\text{C}_2\text{H}_2\text{CuO}_4 \cdot \text{H}_8\text{O}_4$	1.831	124.4
$\text{C}_2\text{H}_2\text{CoO}_4 \cdot \text{H}_4\text{O}_2$	2.118	87.3
$\text{C}_2\text{H}_2\text{NiO}_4 \cdot \text{H}_4\text{O}_2$	2.155	85.8
$\text{C}_2\text{H}_2\text{ZnO}_4 \cdot \text{H}_4\text{O}_2$	2.205	86.6
$\text{C}_2\text{H}_2\text{ZnO}_4$	2.368	65.5
$2(\text{C}_2\text{H}_2\text{SrO}_4 \cdot \text{H}_4\text{O}_2) + \text{C}_2\text{H}_2\text{CuO}_4 \cdot \text{H}_8\text{O}_4$	2.132	306.1
$\text{C}_6\text{H}_6\text{Sr}_2\text{CuO}_{12}$	2.612	194.7
$2(\text{C}_2\text{H}_2\text{BaO}_4) + \text{C}_2\text{H}_2\text{CuO}_4 \cdot \text{H}_8\text{O}_4$	2.747	247.4
CH_2O_2	1.420	32.4
$\text{C}_2\text{H}_4\text{O}_2$	1.230	48.7

Inspection of the table shows that the anhydrous calcium, lead, strontium, manganese, and zinc formates may be regarded as isosteric with formic acid; *i.e.*, the metals in these salts occupy the same volume as the hydrogen they replace.

The difference between the molecular volume of acetic acid (48·7) and that of formic acid (32·4) is $16\cdot3 = \frac{32\cdot4}{2} = \frac{48\cdot7}{3}$. It follows therefrom that O_2 in these acids occupies the same volume as CH_2 . The volume-constitution of the acids is represented by the formulæ:—

$$\begin{aligned} C_2H_4O_2^3 &= 48\cdot76 = 9 \times \overline{5\cdot42} \\ C_1H_2O_2^3 &= 32\cdot40 = 6 \times \overline{5\cdot40} \end{aligned}$$

and, accordingly, the volume-constitution of the five salts mentioned above is—

$$C_2H_2R_2O_4^3 = 12 \times \overline{5\cdot40} = 64\cdot8 \text{ (R = Ca, Pb, Sr, Mn, or Zn).}$$

The hydrated formates contain the anhydrous salt as such, and the water partly as $H_2O_1^1$, and partly as $H_2O_1^1$. The author has previously shown that manganese and zinc sulphates, selenates, and chromates contain water as $H_2O_2^2$; and the same holds good of zinc, cobalt, and nickel formates. He has further shown that manganese sulphate contains water as $H_4O_2^3$, which is true also of manganese formate.

Anhydrous sodium formate and the hydrated double formates of strontium and copper, and of barium and copper, appear to be anomalous in their volumes. J. R.

Volumetric Determination of the Chemical Influence of Mass. Part III.—**On the Mass-influence of Water.** By W. OSTWALD (*J. p. Chem.* [2], 22, 305—322).—Rose showed that water when added in increasing proportions to acid sulphates, produces a gradually augmented decomposition, until at last the separation into neutral salt and free acid becomes complete. The author in the present paper states the results obtained by mixing solutions of sodium sulphate of varying strength with sulphuric acid in different states of dilution, and then measuring the resulting alteration of volume. Four sodium sulphate solutions were mixed with four dilute acid solutions, and each in five different proportions, so that eighty combinations in all were made. The experiments were tried in duplicate, and are tabulated with the statement for each of the chemical formula, the specific volume, the sum of the volume of the components before reaction, the volume after reaction, and the alteration of volume occurring during reaction, representing expansion (+) or contraction (—).

It was found that no relation existed between the alteration of volume produced by the mixture of the same proportions of the sulphate and acid in different states of dilution, and even in the same state of dilution no relation is noticeable; but since the specific volumes in such cases are identical, it follows that such liquids have a similar arrangement of their constituents, and that the final chemical equilibrium is independent of the original distribution of the sulphate, the

acid and the water, provided that after mixture their proportions are the same. Hence the different distribution of the water before mixture gives rise to a different volume change, and the water present in each solution influences the other solution.

The mutual influence of the solutions on one another may be:—(1) The two dissolved substances distribute themselves through the water present, so that the water combined with one is without influence on the other; (2) the whole quantity of water present may influence each substance, so that the water present in each solution acts on the other solution as pure water would do; or (3) both actions may occur simultaneously, each substance uniting with a definite quantity of water, and the excess of water acting on both bodies.

The author considers the third case the most probable, but he has obtained, by calculation from his experimental results, numbers which correspond fairly with the second assumption, and which explain fully the different volume changes noticed when the same proportions of the substances are mixed, but with different distribution of the water.

It is also shown that as the proportion of water increases the formation of acid sulphate decreases.

The bearing of these experiments on the theory of Guldberg and Waage is also considered. According to this theory, the intensity of chemical affinity is proportional to the product of the masses of the bodies which act on one another; accordingly the amount of acid sulphate produced should be the same whatever weights of sulphate and acid are employed, provided the product of those weights is unaltered. The author finds this result borne out by his experiments when strong solutions are used, but with weak solutions the quantity of acid sulphate formed is greater when excess of sulphate is employed than with excess of acid. This difference is attributed to the disturbing influence of the water, the acid having a greater affinity for water than the sulphate has, whence it follows that the acid when in excess is more weakened in its influence than the sulphate is. F. C.

Union of Bodies by Pressure. By W. SPRING (*Ann. Chem. Phys.* [5], 22, 170—217).—In 1850 Faraday discovered that when two pieces of ice are pressed against one another they unite. The nearer the temperature of the two masses to the melting point, the more readily does the union take place. He considered that the phenomenon was a property peculiar to ice. The author enumerates and discusses all the most important theories which have been advanced in explanation of the fact, commencing with that of James Thomson.

He has made a series of experiments on the welding of bodies under pressure, and in order to bring in contact larger surfaces of the substances operated upon, he has employed the bodies in the form of powder.

The following are the results obtained by him:—

I. *Metals.*

Name of metal.	Pressure employed.	Result obtained.	General observations.
1. Lead. (filings) .	2,000 atmos.	Solid block. Sp. gr. 11.501.	Sp. gr. of ordinary lead, 11.3. No trace of powder could be seen with the microscope.
	5,000 "	Behaves like a liquid. Flows through all interstices of the apparatus.	
2. Bismuth (powder)	6,000 "	Solid block. Sp. gr. 9.89. Crystalline fracture.	Sp. gr. of ordinary cast bismuth, 9.9.
3. Tin (powder) ..	3,000 "	Solid block.	Crystalline fracture.
	5,000 "	Appears liquid.	
4. Zinc (powder).	5,000 "	Solid block	
	7,000 "	Appears semi-liquid.	
5. Aluminium (filings)	6,000 "	Solid block. Sp. gr. 2.562.	Sp. gr. of cast metal, 2.562.
6. Copper (filings)	6,000 "	Solid block.	The surface has a metallic lustre, but the centre is powdery.
7. Antimony (powder)	5,000 "	Non-homogeneous block.	
	Above 5,000 "	Solid block.	Resembles antimony.
8. Platinum (spongy)	5,000 "	Non-homogeneous block.	
	Above 5,000 "	Non-homogeneous block.	Complete union of the particles could not be obtained under any pressure.

The author remarks that the relative disposition of the above metals to weld together is in inverse proportion to their hardness. The hardness of metals becoming less as the temperature rises, it can be inferred that they will be more easily compressed at higher temperatures.

II. *Metalloids.*

Name of substance.	Pressure employed.	Result obtained.	General observations.
1. Sulphur (prismatic)	5,000 atmos.	Solid block. Sp. gr. 2.0156. M. p. 115° C.	Transformed into octohedral sulphur. Sp. gr. 2.05. M. p. 111.114°.
Sulphur (plastic)	6,000 "	Solid block	Transformed into the octohedral variety.

II. *Metalloids*—(continued).

Name of substance.	Pressure employed.	Result obtained.	General observations.
Sulphur (octohedral)	3,000 atmos.	Solid block	Octohedral.
2. Phosphorus (amorphous)	6,000 „	Non-homogeneous block.	On the surface of the block are glistening steel-grey scales, probably a metallic modification of phosphorus. It was noticed with regard to sulphur that under pressure it always assumed that form which has the greatest specific gravity. The metallic modification of phosphorus has also the highest sp. gr.
3. Carbon (amorphous)	—	—	Remained unchanged under the greatest pressure that could be applied to it.
Carbon graphite (powder)	5,500 „	Solid block.	Resembles natural graphite.

III. *Oxides*.

Name of substance.	Pressure employed.	Result obtained.	General observations.
1. Manganese dioxide (powder)	5,000 atmos.	Solid block	Crystalline fracture. Resembles natural pyrolucite.
2. Alumina	5,000 „	„	Translucent. Resembles in appearance halloysite.
3. Oxide of mercury (yellow)	4,000 „	Non-homogeneous block.	Surface covered with glistening laminae. The centre of the block remained powdery. Small drops of mercury are formed by the action of the oxide on the iron of the apparatus.
Oxide of mercury (red)	—	—	Behaves like the yellow.
4. Silica	—	—	No union of the particles took place under the greatest pressure.

IV. *Sulphides.*

Name of substance.	Pressure employed.	Result obtained.	General observations.
1. Zinc sulphide..	5,000 atmos.	Solid block	Crystalline. Resembles the natural blende.
2. Lead sulphide.	6,000 "	"	Crystalline. Resembles galena.
3. Arsenic sulphide	6,000 "	"	Crystalline fracture.
4. Mercury sulphide	}	—	{ Do not weld, but agglomerate.
5. Iron sulphide..			

V. *Salts. A.*

Name of salt.	Pressure employed.	Result obtained.	General observations.
1. Ammonium chloride	4,000 atmos.	Solid block	Hard; as regards transparency resembles gelatin.
2. Potassium chloride	5,000 "	Transparent block.	
3. Sodium chloride	—	Translucent block.	
4. Lead chloride..	—	Hard opaque block.	
5. Mercuric chloride	—	Hard opaque block.	
6. Potassium bromide	5,000 "	—	Resembles the chloride.
7. Lead bromide.	—	—	Resembles the chloride.
8. Potassium iodide	—	—	Resembles the chloride.
9. Mercuric iodide	4,000 "	Semi-transparent block.	

B. *Sulphates.*

Name of sulphate.	Pressure employed.	Result obtained.	General observations.
1. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (powder)	3,000 atmos.	Solid block.	Becomes liquid.
2. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (powder)	5,000 "	—	
3. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (powder)	5,000 "	Hard block.	
4. $\text{Al}_2(\text{SO}_4)_3 \dots$	6,000 "	Hard transparent block.	Very incomplete union. Resembles $\text{Al}_2(\text{SO}_4)_3$.
5. Ammonia alum	—	—	

B. *Sulphates*—(continued).

Name of sulphate.	Pressure employed.	Result obtained.	General observations.
6. Gypsum.....	—	—	Incomplete.
7. Aluminium sulphate	} Anhydrous	—	{ It is worthy of remark that all these are amorphous, and when hydrated do not crystallise well.
Zinc sulphate..			
Lead „ ..			

C. *Nitrates*.

Name of nitrate.	Pressure employed.	Result obtained.	General observations.
1. Potassium nitrate	2,000 atmos.	Translucent block.	
2. Sodium nitrate	3,000 „ —	— —	Becomes plastic. Resembles the preceding.

D. *Carbonates*.

Name of carbonate.	Pressure employed.	Result obtained.	General observations.
1. Sodium carbonate (anhydrous)	5,500 „	Opaque block	The separate grains can still be seen.
2. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	5,500 „	Transparent block.	
3. Zinc carbonate	7,000 „	Hard opaque block.	Resembles writing chalk. Imperfect, though harder than chalk.
4. Chalk	5,000 „	Hard block	
5. Iceland spar...	6,000 „	—	No union under any pressure.
6. Lead carbonate	—	—	

E. *Thiosulphates*.

Name of salt.	Pressure employed.	Result obtained.	General observations.
1. Sodium thio-sulphate	4,000 atmos.	Transparent glassy block.	Under greater pressure it becomes liquid.

F. Phosphates, &c.

Name of phosphate.	Pressure employed.	Result obtained.	General observations.
1. $\text{Na}_2\text{HPO}_4 \cdot 10\text{H}_2\text{O}$	5,000 atmos.	Transparent block.	Porcelain-like fracture.
2. Aluminium phosphate	6,000 "	Translucent hard block.	
3. Crystallised borax	7,000 "	Hard block	Incomplete.
4. Fused borax	—	—	Very incomplete.
5. Glass.....	6,000 "	—	The particles commence to unite.

VI. Carbon Compounds.

Name of substance.	Pressure employed.	Result obtained.	General observations.
1. Wax.....	260 atmos.	Perfect union	Temperature, 13°.
	700 "	—	Becomes liquid.
2. Paraffin	260 "	Homogeneous block.	More transparent than the ordinary.
	2,000 "	—	Becomes liquid.
3. Camphor	3,000 "	Very transparent block.	
4. Gum arabic ..	5,000 "	Translucent block.	Plastic.
5. Starch.....	6,000 "	Hard semi-transparent block.	Fracture resembling porcelain.
6. Cotton-wool (dry)	10,000 "	—	No union of the fibres.
Cotton-wool (moist)	6,000 "	Solid mass	Loses its organised texture.
7. Sealing wax..	5,000 "	Solid block	Temperature, 16°.
8. Resin	—	—	Welds with great difficulty.
9. Eosine (red powder)	4,000 " *	Hard green block.	
10. Coal	6,000 "	Solid block.	
11. Turf.....	6,000 "	Brilliant black block.	Resembles coal. Becomes plastic above 6,000 atmos.
12. Bone-black ..	—	—	No union under any pressure.
13. Oxalic acid...	—	Semi-transparent.	Welds easily.
14. Sugar	6,000 "	—	Imperfect.
15. Potassium acetate	4,000 "	Hard block	Commences to be liquid.
16. Tartaric acid .	—	—	Less perfect than oxalic acid.
17. Potassium ferrocyanide	5,000 "	Hard yellow block.	Transparent.
18. Potassium ferricyanide	—	—	Much more easily than the preceding.

VII. *Chemical Reactions induced by Pressure.*

Chemical actions can be divided into two classes; one, in which the sum of the volumes of the products is greater than the sum of those of the initial substances; and a second, in which it is less. It has been shown by Pfaff that the action of nitric acid on calcespar is arrested under a pressure of 60 atmospheres. The author has investigated the effect of pressure on the reactions of the second class. The following are the results obtained by him:—

1. On subjecting a mixture of copper filings and sulphur to a pressure of 500 atmos. there was complete combination, crystallised copper sulphide being formed. The 138 vols. of Cu and S became 100 vols. of Cu_2S .

2. A mixture of mercuric chloride and copper gave under 5,000 atmos. cuprous chloride and mercury.

3. A mixture of dry potassium iodide and mercuric chloride gave under 2,000 atmos. mercuric iodide and potassium chloride.

The author has proved that reactions of the first class do not take place under pressure.

1. A mixture of sulphide of mercury and potassium iodide was unchanged.

2. A mixture of ferrous sulphide and sulphur does not give FeS_2 .

3. A mixture of mercury and sulphur was unchanged.

4. A mixture of dry tartaric acid and sodium carbonate gave no trace of carbonic anhydride. On the other hand, a mixture of sodium carbonate and arsenic pentoxide gave carbonic anhydride and sodium arsenate.

The author draws the following conclusions from his experiments:—

1. That the property which bodies possess of welding together under pressure, appears to be a function of their hardness.

2. That this property is possessed by crystalline substances only. Amorphous allotropic modifications of crystalline bodies are considered to belong to this class.

The apparatus employed to effect the compression consists of a powerful lever, which forces a piston into a cylinder. The necessary pressure is obtained by adding weights to the extremity of the lever.

J. I. W.

Transpiration of Vapours. By L. MEYER and O. SCHUMANN (*Ber.*, 14, 593—599).—A continuation of the author's former researches (*Abstracts*, 1878, 368). As the friction constant varies considerably with the temperature, the vapours were allowed to transpire at their boiling point and at normal pressure. The experiments show that in equal times approximately equal volumes of all the vapours examined transpired, the friction constants under these conditions being approximately equal, varying from 0.000150 to 0.000174 (centimetre, second). The following table contains the coefficient n of friction for the ethereal salts, multiplied by 10^6 :—

	Methyl.	Ethyl.	Propyl.	Isopropyl.	Amyl.
Formate.....	173	156	159	172	160
Acetate	152	152	160	155	—
Propionate.....	150	158	153	164	158
Butyrate	159	160	164	167	155
Isobutyrate	152	151	153	158	155
Valerate.....	163	165	167	154	—

Acetic acid ($n \times 10^6 = 163$) and butyric acid ($n \times 10^6 = 150$) have also the same friction coefficient as those of the ethereal salts.

The numbers for the transpiration in the gaseous state show the same relation to one another as those found by Kellstab (Inaug. Diss., 1868) for the transpiration in the liquid state. By means of the friction coefficient, the authors have also determined the molecular volume according to a method described in *Annalen*, 1867, Suppl. Band 5, 129. Taking the mean of the values obtained for the ethereal salts of equal molecular weight, and comparing them with the relative values of the molecular volumes as found by Kopp, the following concordant numbers are obtained by either method (methyl formate being taken as unity):—

	Calculated from friction constant.	Kopp.
$C_2H_4O_2$	1	1
$C_3H_6O_2$	1.522	1.344
$C_4H_8O_2$	1.840	1.688
$C_5H_{10}O_2$	2.039	2.031
$C_6H_{12}O_2$	2.391	2.374
$C_7H_{14}O_2$	2.602	2.718
$C_8H_{16}O_2$	2.828	3.063
$C_9H_{18}O_2$	3.413	3.406

From these numbers it follows that the molecular volumes deduced from the friction coefficient bear the same relation to one another as the molecular volumes in the liquid state.

On comparing the author's numbers with those calculated for gases from Graham's researches, it is found that the former are too small, but the discrepancy is easily explained if the variability of the friction coefficient with temperature is taken into account. A solution of the fact that the friction coefficient is less the higher the temperature, lies in the consideration that the values calculated by the author's method for the molecular volumes do not exactly represent the space filled by the mass of the particle, but rather the space which another colliding particle cannot penetrate.

V. H. V.

Smoke and Vapour under the Microscope. By L. J. BODASZEWSKY (*Landw. Versuchs.-Stat.*, 26, 325).—Smoke of burning paper, wood, cigar, &c., collected in a cell and viewed with a magnifying power of 100 diameters, shows small oscillating particles of about 0.0002 to 0.0003 mm. diameter. Vapour of nitric acid, sulphuric acid, phosphoric acid, sulphur, &c., produced under the microscope by a platinum wire heated galvanically, give similar moving particles; water vapour, however, shows only a faint moving glimmer.

J. T.

Inorganic Chemistry.

Chlorine Trioxide. By K. GARZAROLLI-THURNLACKH (*Ber.*, **14**, 28).—The author finds that when this gas is decomposed, the expansion it undergoes is almost exactly equal to half the volume of the oxygen set free. Hence, he concludes that the so-called chlorine trioxide is really a mixture of tetroxide and free chlorine, and that euchlorine is a mixture of the tetroxide and oxygen. Pure chlorine trioxide would show on decomposition an expansion equal to the volume of oxygen set free. J. R.

The Invariable Production, not only of Ozone and Hydrogen Peroxide, but also of Ammonium Nitrate, in the Ozonation of Purified Air by Moist Phosphorus. By A. R. LEEDS (*Chem. News*, **43**, 97—100).—The conclusions drawn from the results of this extended research are the following:—

1. Both ozone and hydrogen peroxide are produced during the ozonation of purified air by moist phosphorus, in the ratio approximately of one molecule of the latter to one of the former.

2. Both bodies are evolved, the suspended hydrogen peroxide passing through a series of wash-bottles without undergoing any but a slight absorption, and being present in the evolved gas in nearly the same ratio as that which it held to the ozone when originally produced.

3. Along with these two bodies, and as a necessary part of the same series of reactions incident originally to the setting free of nascent oxygen, a certain amount of ammonium nitrate is invariably produced. This last is altogether detained in the water of the ozonator and of the wash-bottles. D. B.

Gay-Lussac's Hypochloronitric Anhydride. By H. GOLDSCHMIDT (*Annalen*, **205**, 372—380).—Baudrimont in 1846 (*Ann. Chim. Phys.* [3], **17**) claims to have prepared a body, NO_3Cl_2 ($\text{O} = 8$) by distilling *aqua regia*. Gay-Lussac two years later (*Ann. Chim. Phys.* [3], **23**) repeated this experiment and obtained a body, NOCl_2 , which he called *acide hypochloronitrique*.

The author considers that this body is probably a mixture of nitrosyl chloride and chlorine. When oxygen is replaced by its equivalent amount of chlorine, the boiling point is as a rule raised, but the substance obtained by distilling *aqua regia* boils at -7° (Gay-Lussac), whereas nitrogen peroxide, NO_2 , boils at 22° . It is also noteworthy that this product has almost the same boiling point as nitrosyl chloride, NOCl , -8° (Tilden), -5° (Müller). Again, the author in three experiments found 68·23, 60·77, and 67·36 per cent. of chlorine, theory for NOCl_2 demanding 70·3.

By fractionally distilling his product, he obtained a body having 57·39 per cent. of chlorine as a mean of three experiments, NOCl re-

quiring 54.2. The vapour-density of his product and the determination of the amount of chlorine in the actual substance experimented on, confirms the conclusion that the product obtained by distilling *aqua regia* is a mixture of nitrosyl chloride and free chlorine.

F. L. T.

Existence and Properties of Phosphorus Pentiodide. By F. HAMPTON (*Chem. News*, **42**, 180).—It is usually said that phosphorus unites with iodine in but two proportions, forming a di-iodide and tri-iodide, but no pentiodide corresponding to the higher bromide or chloride.

In Gay-Lussac's work on iodine, however, containing the results of the experiments made by him on Courtois' newly discovered element, he states that on bringing together 1 part of phosphorus and 16 iodine, a grey-black crystallised substance was formed fusible at 29° , and producing on contact with water a colourless solution containing hydriodic and phosphorous acids; while 1 part phosphorus with 24 of iodine gave a black substance, fusible in part, at 46° , and dissolving in water with elevation of temperature, the solution containing hydriodic and *phosphoric* acids, and exhibiting a dark brown colour from the presence of free iodine.

The author has examined the latter of these reactions with a view of ascertaining, if possible with certainty, whether phosphorus pentiodide can really be obtained. He made several experiments with concordant results. In some, the two elements were brought together in a neutral atmosphere of pure nitrogen, without any other additional substance being present, but it was found difficult to regulate the violence of the action and to prevent too great a rise of temperature. In others, therefore, carbon bisulphide was used to dissolve and so dilute the phosphorus before the addition of the iodine; and with proper precautions this was found to produce no change in the final result, whilst rendering the process much more easily manageable.

From the author's experiments it appears that phosphorus pentiodide can be obtained by the direct union of its elements.

D. B.

Solid Compounds of Boron and Hydrogen. By REINITZER (*Wien. Akad. Ber.*, **82**, 736).—After observing that boron is the only known elementary substance (Berzelius) soluble without change in water, the author of this paper describes some experiments made to obtain the theoretically possible body BH_3 .

For this purpose potassium boride was made and added in small portions to a large volume of dilute hydrochloric acid, and the precipitated green-brown amorphous powder washed finally with alcohol and dried at 120° .

This dried substance was introduced into small bulb-tubes with drawn-out points, and on applying heat to the portion containing the substance, it exhibited an appearance of glowing at a certain temperature, and a gas was given off which burnt with a green-edged flame. As this seemed to indicate a hydrogen compound, some combustions were made with oxide of copper, which undoubtedly show the

existence of a hydrogen compound, approximating to the formula $B_{3.32}H$.

Solid compounds of hydrogen with phosphorus and arsenic are formed under similar circumstances. It is very probable that the supposed solubility of boron in water is really due to a hydride.

W. R. H.

Preparation of Silicon Oxychlorides. By L. TROOST and P. HAUTEFEUILLE (*Bull. Soc. Chim.* [2], **35**, 360, 361).—On passing a heated mixture of chlorine with one-half or one-fifth its volume of oxygen, over crystalline silicon, a mixture of silicon oxychlorides and dichloride is obtained. The heat evolved is sufficient to continue the reaction when once it has commenced. Too high a temperature is to be avoided, since the vapours of the dichloride and oxychlorides form a thick cloud which is only condensed with difficulty. The action of the mixture on silicon is not so violent as that of chlorine alone; but whether silicon tetrachloride is first formed and chlorine afterwards displaced in it, or the oxygen and chloride both unite directly with the silicon, remains to be proved.

L. T. O'S.

Composition of Sodium Hyposulphite. By A. BEERNTHSEN (*Ber.*, **14**, 438—440).—In order to ascertain the composition of sodium hyposulphite, the crude product of the action of zinc on sodium hydrogen sulphite was mixed with barium chloride to remove sulphites and sulphates from the solution. By converting the hyposulphite in the filtrate into sulphate, by means of iodine, it was found that 3 atoms of iodine were required to convert one atom of sulphur in the hyposulphite into sulphuric acid.

Two molecules of ammoniacal cupric sulphate, or one atom of oxygen, were required to convert two atoms of sulphur in the hyposulphite to sulphite. The atoms of sodium and sulphur were found to be in the proportion of 1 : 1; hence the formula for sodium hyposulphite is $NaSO_2$ or $Na_2S_2O_4$.

W. C. W.

Nature of the Insoluble Form of Soda existing in the Residue left on Causticising Sodium Carbonate Solutions with Lime. By W. SMITH and W. T. LIDDLE (*Chem. News*, **43**, 8).—The authors tried the following experiments with the crystalline precipitate obtained by mixing solutions of sodium carbonate and lime-water and warming, also with ordinary "lime-mud" from the causticising pan of an alkali works after the usual washing and draining:—

1. The effect of ignition upon the crystalline precipitate, prepared as above, and upon the "lime-mud" of the soda works.

2. The effect of long-continued boiling with water.

3. The effect of boiling with some saline solution, as, for example, with sodium sulphide.

The practical portion of the results shows that in the "causticising process" the residual soda is kept in circulation in the process, and so is not lost, the lime-mud being drained and used again in the black-ash mixture. In some works, however, where black-ash is not made, e.g., soap-works, causticising from soda-ash, &c., an average loss of

about 7.25 per cent. Na_2CO_3 of the dry residue, or 4.7 per cent. of the washed and well-drained mud, is sustained. In the black-ash process it is evident that an adequate improvement, by which a minimum amount of calcium carbonate is used in the black-ash mixtures, must effect an improved yield of soda on lixiviation, a smaller retention as insoluble compound in the soda-waste occurring. D. B.

Crystallised Double Sulphate of Calcium and Sodium. By C. W. FOLKARD (*Chem. News*, 43, 6).—In the Welsh process of manufacturing sodium acetate, during the evaporation of the liquor formed by the double decomposition of calcium acetate and sodium sulphate, a salt separates out in the form of micaceous spangles, which are greasy to the touch, like steatite. They are of a light brown colour, due to tarry compounds dissolved in their mother-liquor. After removal of adhering acetate by alcohol, pressing between blotting-paper and drying over calcium chloride, they have the following composition:—

	By analysis.	Theory.
Ca.....	14.1	14.39
Na_2	16.8	16.55
$(\text{SO}_4)_2$	68.7	69.06

On gently igniting, the salt is unchanged, but on heating to bright redness the crystalline form is destroyed. It is insoluble in alcohol and in concentrated solutions of sodium acetate, but is decomposed by weak solutions and by water. On treatment with water, or solution of sodium acetate of sp. gr. 1.150 and under, the salt is decomposed into sodium sulphate, which passes into solution, and calcium sulphate, the latter, however, still containing soda. The formation of this salt may explain why calcium sulphate obstinately retains sodium sulphate in double decomposition, which is only partially extracted even by boiling water. This is a source of considerable loss in certain manufacturing operations. D. B.

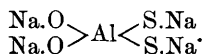
Amount of Water of Crystallisation of Hydrated Strontium Nitrate. By A. L. BAKER (*Chem. News*, 42, 196).—It is mentioned that with regard to the extent of hydration in this salt, most recent writers give 4 mols. H_2O , while some give 5 mols. H_2O , as formerly found by Laurent and earlier experimenters. The author made a number of experiments with different rates of cooling and of evaporation at uniform temperature, and at temperatures ranging from 2° to 32° , with a view of ascertaining whether by these variations more than one hydrated salt can be formed. The result was a negative one, either the anhydrous salt, or that with 4 mols. H_2O being obtained. As regards the limit of temperature at which the hydrated nitrate is obtainable, the author states that by slow evaporation at 32° of a saturated solution, he obtained, in one instance, a mixture of anhydrous and hydrated crystals. D. B.

Composition of Ultramarine. By H. ENDEMANN (*Chem. News*, 42, 204—206).—Most authors consider ultramarine-blue to be com-

posed of silica, soda, alumina, sodium monosulphide, and sulphur, the latter also in chemical combination, as it cannot be removed by solvents unless these act chemically at the same time. It is mostly considered as being united with sodium sulphide, forming polysulphides. All these substances are required to form ultramarine, but the author does not consider them all as serving the same purpose. To simplify matters, he regards one portion of the soda and alumina, and the whole of the silica, merely as a vehicle necessary for the preparation and existence of ultramarine, as they serve to facilitate the reaction in the first instance, whilst later in the process they act in protecting the product against too powerful oxidation. This silicate may have a varying composition, and for this reason alone it would be difficult to correctly ascertain its quantitative relation to what may be called the colour-nucleus. This we may suppose in ordinary ultramarine-blue to be:— $\text{Na.S.S.AlO.O.AlO.SNa}$, and in Heumann's ultramarine-blue:— NaS.AlO.O.AlO.SNa .

The first of the two, under the influence of acid, will give two-thirds of the sulphur as such, whilst one-third will be obtained as H_2S . The latter (Heumann's) will give half as sulphur and half as H_2S . Whilst, therefore, Heumann's ultramarine-blue must be considered the purest, it will be seen that ordinary ultramarine-blue may contain more sulphur in combination.

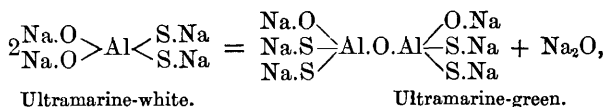
I. Ultramarine-white. The author assigns to this a constitution analogous to that of the neutral sodium silicate, a portion equal to half of the oxygen being substituted by sulphur:—



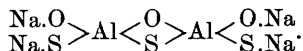
This constitutional formula includes the possibility of partial substitution of the aluminium by silicon.

By the action of sulphurous acid gas ultramarine-white is first converted into ultramarine-green, two atoms grouping together with loss of Na_2O , forming the first coloured compound:—

II. Ultramarine-green—



and this by the action of oxygen, which forms sodium sulphate with further loss of Na_2S , is converted into the jet-green compound:—



Aqueous acids, with the first green, would produce $3\text{H}_2\text{S}$ to S , and with the second green $2\text{H}_2\text{S}$ to S . It is even possible that by the combined action of oxygen and sulphurous acid an interpolated green may be obtained, the sulphur for the sulphate being then furnished by the sulphurous acid, so that in this case nothing but sodium is removed.

III. Ultramarine-blue is produced by the action of sulphurous acid

and oxygen on the green, whereby more sodium is removed and the middle sulphur is interpolated in one of the groups ending with Na. The sodium is converted into sulphate. The action of chlorine will produce the same product, leaving $\text{NaS.S.AlO.O.AlO.SNa}$.

This product should yield, with aqueous acids, $\text{H}_2\text{S} + \text{S}_2$. Hydrochloric acid gas would form H_2S , 2NaCl , and NaS.AlO.O.AlO.SNa , which latter substance, with aqueous acids, would yield $\text{H}_2\text{S} + \text{S}$. This is Heumann's ultramarine-blue, which has only once been prepared as pure as this, owing, undoubtedly to the superior care used by Heumann in its production. Further removal of sodium, and perhaps partial substitution of sulphur by oxygen, seem then to form the violet, the so-called red, and the yellow. The author could not find sufficient analytical data to justify formulæ for these compounds. D. B.

Properties and Chemical Character of Glucinum. By L. F. NILSON and O. PETTERSSON (*Chem. News*, 42, 297—299).—The authors obtained metallic glucinum by heating the chloride to redness with sodium in a wrought-iron crucible, hermetically closed with a screw-plug. The reduced metal was partly fused into globules, partly formed of aggregations of prismatic crystals, resembling steel in hardness and colour, and had the composition G 86.94, G_2O_3 9.99, Fe 2.08, SiO_2 0.99 = 100; determinations of its specific heat between 0° and 100° , by means of Schüller and Wartha's modification of Bunsen's method, gave 0.4048; atomic heat = 5.64 ($G = 13.8$). By careful analysis of the pure hydrated sulphate, the equivalent of the metal was found to be 4.552, if $O = 8$, or 4.452 if $O = 7.98$, and therefore Lothar Meyer's supposition that the true equivalent might be less than 4.0, is not borne out by facts. Determinations of the molecular heats of the rare earths and their sulphates gave the following values for the atomic heat of oxygen:— Al_2O_3 , 2.35; G_2O_3 , 2.34; Sc_2O_3 , 2.67; Ga_2O_3 , 2.88; In_2O_3 , 3.08. The atomic heat of oxygen is the same in glucina as in alumina, in fact these two oxides are the first members of a group of sesquioxides in which the atomic heat and the atomic volume of the oxygen increase with the atomic weight of the metal. The following determinations at different temperatures show that the specific heat of glucinum increases with the temperature.

Temperature.	Sp. heat.	Atomic heat.
46.35	0.3974	5.46
100.07	0.4246	5.79
214.00	0.4750	6.48
299.50	0.5060	6.90

The increase is, however, not greater than that observed in the case of iron, and is very much less than in the case of the diamond. The authors consider that much weight cannot be attached to Carnelley's calculation of the atomic weight of glucinum from the melting point of its chloride, since this calculation was based on a knowledge of the properties of the salts of only one triad metal, aluminium, the properties of the compounds of the more recently discovered triads being yet unknown. All the authors' experiments led to the conclusion that the true atomic weight of glucinum is 13.65; if this value be accepted,

glucinum does not conform to Mendelejeff's law as at present formulated; in this respect it resembles tellurium, and this fact, together with the difficulty of arranging erbium and ytterbium in those places in the system, which are indicated by their relations to the other earth metals, necessitates a modification and development of the periodic law.

C. H. B.

Rusting of Iron. By T. L. PHIPSON (*Chem. News*, **42**, 286).—With regard to the assertion that iron and steel do not rust when immersed in solutions of soda or potash, the author gives the following explanation: Calvert many years ago showed that the phenomenon of the rusting of iron was due to the presence of carbonic acid, this body forming the *third substance* requisite according to the author's theory of catalysis, to complete the galvanic chain. Without the presence of this carbonic acid or some other *third substance* capable of taking its place, the oxygen cannot combine with iron at ordinary temperatures. A high temperature acts like electricity in promoting the combination. As long as there is free caustic alkali present, of course there can be no carbonic acid, and no rust is formed.

D. B.

Stability of Calomel. By P. HOGAN (*Chem. News*, **42**, 178).—The conversion of calomel into corrosive sublimate by the chlorides of the alkaline metals, and also by the organic acids, has for a long time been a much vexed question: hence the author made a series of experiments to discover the cause of the great discrepancies on this subject, and also to ascertain the correctness of Verne's assertion, that "the danger of acid drinks when using calomel is pure prejudice."

The conclusions drawn from the author's experiments show—first, that calomel is slowly converted into corrosive sublimate by water at the temperature of the body; secondly, that chloride of sodium, citric acid, and sugar greatly promote the conversion of calomel into corrosive sublimate, and hence are more or less dangerous when present in the system with calomel; thirdly, that the discrepancies in regard to the stability of calomel are in part accounted for by taking into consideration the temperature at which the experiments have been conducted (78° F. and 98° F.); fourthly, that at the temperature of the human body calomel is an unstable compound.

D. B.

Atomic Weight of Antimony. By J. P. COOKE (*Sill. Jour.* [3], **19**, 382).—In the determination of the exact composition of antimonious bromide by precipitation of the bromine with silver in presence of tartaric acid, a certain amount of error is unavoidable. If, however, the volumetric process be substituted for the gravimetric, these errors are avoided.

If the atomic weight of antimony were 122, it would require 1.79 grams of silver to precipitate the bromine from a solution of 2.00 grams of antimonious bromide, whilst if the atomic weight of antimony were 120, it would require 1.80 grams of silver.

2.5032 grams of antimonious bromide were dissolved in aqueous

tartaric acid. To precipitate the bromine from this solution, 2.2404 grams of silver would be required if $Sb = 122$, and 2.2529 if $Sb = 120$. The smaller of these two quantities of metallic silver was weighed out and converted into nitrate, and added to the solution of antimonious bromide; 12.4 c.c. of a normal silver solution (1 gram silver per litre) were required to complete the precipitation. The mean percentage of bromine from fifteen gravimetric determinations was 66.6665. $Sb = 120$ requires 66.6666, whilst $Sb = 122$ is 66.2983.

C. W. W.

Incandescence of Cupric Antimonate when heated strongly.

By C. L. ALLEN (*Chem. News*, **42**, 193).—Berzelius has recorded the observation that certain antimonates and antimonites when exposed to a dull red heat, after water of crystallisation has been expelled, present a transient but bright incandescence, looking like combustion, without any change of weight being experienced. The glowing is said to be especially noticeable with the antimonates of copper, cobalt, and zinc. The author found that cupric antimonate produced the phenomenon of incandescence only by strong ignition over a blast (gas) lamp, but that when it occurred it was quite bright and distinct. As the temperature was much above that at which the last of the water was removed, and no further alteration of weight occurred, the author considers that, while there is no reason to suspect any change of chemical relation between the remaining constituents, the phenomenon seems most probably one dependent upon change of physical structure only. With regard to the statement by Berzelius, that cupric antimonate becomes black when merely heated sufficiently to drive off the water, and after ignition and glowing appears white with a slightly greenish tinge, it is thought that probably the salt he experimented with contained an admixture of cupric hydrate. Pure cupric antimonate changes its original pale bluish-green colour on heating to a more and more yellowish-green, finally becoming after incandescence and cooling a pale greenish-grey.

D. B.

Oxidation of Hydrochloric Acid Solutions of Antimony in the Atmosphere.

By J. P. COOKE (*Sill. Jour.* [3], **19**, 464).—When a solution of antimonious chloride containing free acid is exposed to the air, it absorbs oxygen, and is then capable of dissolving more antimony. A solution containing 1.4136 gram antimony with excess of hydrochloric acid dissolved in this way 0.9826 gram in 198 days at a temperature of 15–30°. In another experiment a mixture of 5 grams of finely powdered antimony with 50 c.c. of strong hydrochloric acid and 1 c.c. of dilute nitric acid (5.4 per cent.) was exposed to the air in an open flask. The mixture soon became reddish-yellow, and some antimony dissolved. When the action had apparently ceased, the contents of the flask were shaken, and the solution became colourless. On exposure to the air its colour returned, again disappearing on agitation. These phenomena were repeated for four or five months, until the whole of the antimony was dissolved. In this way the antimony was brought into solution by means of only one-fiftieth the amount of nitric acid theoretically necessary, assuming the *aqua regia* to act in the ordinary manner.

C. W. W.

Atomic Weight of Platinum. By K. SEUBERT (*Annalen*, **207**, 1—50).—Hitherto the atomic weight of platinum has been taken at between 196 and 198, these figures being based on the researches of Berzelius, Davy, Vauquelin, and others, all of which were probably made with impure material. This high atomic weight excluded platinum from its theoretically proper place and order in the series $\text{Os} < \text{Ir} < \text{Pt} < \text{Au}$, this theoretical order having to be reversed, so that $\text{Au} < \text{Pt} < \text{Ir} < \text{Os}$.

The author (*Ber.*, **11**, 1770) has shown that iridium has the atomic weight 192.64, which is less than that of platinum.

In the redetermination of the atomic weight of platinum, platinum chloride solution was treated by v. Schneider's method to separate iridium and other metals of the platinum group, precipitated with ammonium chloride, and reduced to spongy platinum. The compounds employed for the determinations were $\text{K}_2\text{Cl}_2 \cdot \text{PtCl}_4$ and $(\text{NH}_4\text{Cl})_2 \cdot \text{PtCl}_4$. The salts were reduced in a stream of hydrogen at a red heat, the hydrogen being finally replaced by carbonic anhydride.

In addition to the determination of the weight of metallic platinum, the hydrochloric acid produced during the reduction in hydrogen, and, in the case of the potassium salt, the amount of chlorine in combination with potassium were also determined.

By different methods the following numbers were obtained:—

Ammonium platinochloride: mean of 22 platinum determinations gave 194.7506; mean of three chlorine determinations gave 195.33013. Potassium platinochloride: mean of eight platinum determinations gave 194.39190; mean from eight potassic chloride determinations gave 194.49368; mean of three chlorine determinations gave 194.63088.

From these and other analyses, the author gives the atomic weight of platinum as 194.46124.

According to this number platinum takes its proper position in the series $\text{Ir} < \text{Pt} < \text{Au}$, osmium still remaining an apparent exception. Probably its correct atomic weight is 192, instead of, as at present taken, 198.5.

W. R. H.

Chemistry of the Platinum Metals. By T. WILM (*Ber.*, **14**, 629—637).—In order to separate the impurities from the filtrate obtained after precipitation of the platinum as ammonium platinochloride (this Journal, Abstr., 1880, 854), the author proceeds as follows:—

The metals are precipitated by iron, and boiled frequently with hydrochloric acid to extract the copper, iron, and lead, the last traces of copper being removed as copper oxalate by a concentrated solution of oxalic acid. The filtrate obtained is mixed with ammonium chloride and alcohol, which precipitates the mixed chlorides of rhodium and lead. After these have been separated, the solution is evaporated, when small quantities of ammonium platinochloride with larger quantities of the dark garnet-red ammonium rhodio-chloride crystallise out. The rhodium salt has the constitution $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O}$ or $\text{Rh}_2\text{Cl}_6 \cdot 4\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$, according to the conditions of the evaporation. On heating the double salts in hydrogen, pure rhodium is obtained as

a grey glistening mass, which surpasses even palladium in the readiness with which it absorbs hydrogen. The oxidation of rhodium does not seem to depend entirely on the admixture of other metals, but to be a peculiar property of pure rhodium itself. An attempt to separate the platinum metals from copper and lead by passing a current of hydrogen through a solution freed from copper was unsuccessful, for the precipitate contained appreciable quantities of other metals besides those of the platinum group.

V. H. V.

Mineralogical Chemistry.

Artificial Production of Hollow Pseudomorphs. By A. KNOP (*Jahrb. f. Min.*, 1881, 1, Ref. 178).—Pseudomorphs of various rhombohedral carbonates, after calcite, may be formed by displacing a substance comparatively soluble in carbonic acid (CaCO_3), in this case by a less soluble compound. Similarly, when a crystal of ammonia iron alum is immersed in a solution of ammonia aluminium alum, hollow pseudomorphs of the latter, after the former, are obtained. When a crystal of the more soluble ammonia iron alum is laid in a cool, somewhat supersaturated or nearly saturated solution of ammonia aluminium alum, growth takes place, but not in the form of simple deposition, the crystals on the other hand being first corroded, and the salt previously in solution being deposited in the hollows thereby produced in small crystals which gradually grow and unite into a thin coherent transparent film, whereby the further access of the solution to the crystals is prevented. If such a film is formed on each surface of the crystal—which, however, seldom takes place—the crystal is completely protected from the further action of the solution, and the newly-formed incrustation keeps on growing. When, on the other hand, a crystal is laid with its octohedral face on the bottom of the vessel, the coating formed thereon is incomplete, and consequently the solution still has access to the crystal, which gradually disappears; and as the quantity of iron alum dissolved is greater than that of the aluminium alum deposited, a hollow pseudomorph is formed after all the iron alum has disappeared. From this mode of action, the author infers that saturated solutions of the iron and aluminium alums can never form a saturated mixture. Klocke (*Zeitschr. f. Kryst.*, 2, 756) had previously shown that other two solutions, when mixed in equal volumes, form a supersaturated mixture. If the surface of the crystal does not lie immediately on the bottom of the vessel, a saturated solution of the aluminium alum may enter continuously in excess within the crust, and from this solution crystals may separate, and fill the interior more or less completely as a porous mass having no definite structure. H. W.

Remarks on the Native Iron of Greenland. By F. WÖHLER (*Jahrb. f. Min.*, 1879, 832—834).—L. Smith, while pointing out the

probable terrestrial and not cosmical origin of these iron masses, quoted briefly an analysis by the author, but without describing the peculiarities of the specimen. The author therefore wishes to repeat his description. It is a portion of the mass weighing 20 lbs., found by Nordenskiöld near Ovivak, and whilst other samples of this native iron from Greenland soon fall to pieces, this has remained for seven years quite unchanged. A polished surface shows it to consist of a dark ground-mass, penetrated by a fine network of a lustrous white metal. It is only slowly and partially attacked by acids. Heated in a current of hydrogen, a large quantity of water is formed, and it loses 11.09 per cent., *i.e.*, of oxygen. Heated in a vacuum in an iron tube, it evolves more than a hundred times its volume of carbonic oxide and finally some carbonic anhydride. In both cases, the residuary masses have a uniform and a lighter colour, are attacked violently by hydrochloric acid, and consist of metallic iron. The oxygen is undoubtedly combined with the iron, probably as ferrous oxide, and on this supposition its composition is:—

Fe.	FeO.	FeS.	Fe ₂ P.	Ni & Co.	C.	Si, Cr, Cu.
36.35	49.90	7.75	0.69	1.66	3.69	0.08 = 100.13
H. B.						

Composition of Magnetic Pyrites. By H. HABERMEHL (*Jahrb. f. Min.*, 1880, 2, Ref. 303).—To decide the question whether magnetic pyrites is a definite chemical compound, or an isomorphous mixture of two different iron sulphides, or lastly, a mechanical mixture of FeS with FeS₂ or Fe₃S₄ or S, the author pulverised pure magnetic pyrites from Bodenmais, immersed it in water, separated the magnetic particles by means of a magnet, repeating the treatment on the portions thereby separated, and analysed the most highly magnetic portions obtained by this last operation. The result showed that in 14 samples thus obtained, the percentage of iron varied only between 60.373 and 60.708 per cent., and that of sulphur between 39.214 and 39.627. Dividing these numbers by the respective atomic weights, the ratio of the number of atoms of iron to that of sulphur is confined between the limits 1 : 1.1289 and 1 : 1.153, the former giving a result between Fe₇S₈ and Fe₈S₉, the latter agreeing nearly with the formula Fe₇S₈. The magnetic pyrites of Bodenmais is therefore not a mechanical mixture, but is of uniform composition in all its parts. The mean atomic ratio deduced from the fourteen analyses above-mentioned is 1 : 1.13933 or 7 : 9.751, that is to say, nearly 7 : 8; hence the formula is Fe₇S₈.

The author also finds, from a series of experiments, that magnetic pyrites, when ignited in a stream of hydrogen, continually gives off sulphur till, after prolonged ignition, it attains nearly the composition Fe₈S₉, which may be regarded as a mixture of FeS with metallic iron.

Lastly, from a comparison of all the published analyses of magnetic pyrites, the author concludes that the atomic ratios of Fe : S in this mineral vary between 1 : 1.061 and 1 : 1.1902, the former agreeing nearly with the formula Fe₁₆S₁₇, the latter with Fe₈S₉, whence he finally comes to the conclusion—previously arrived at by Rammelsberg

—that the composition of magnetic pyrites may be represented by the general formula $\text{Fe}_n\text{S}_{n+1}$, in which n may vary from 5 to 16.

H. W.

Guejarite: a New Mineral Species discovered in the District of Guejar, in the Sierra-Nevada, Andalusia: by E. CAMENGE.—**On the Crystalline Form of Guejarite:** by C. FRIEDEL (*Jahrb. f. Min.*, 1881, **1**, Ref. 12).—This mineral is found in a small vein of ferrous carbonate, forming steel-grey shining tables, having a bluish reflex. Its analysis gave 25.0 per cent. S, 58.5 Sb, 15.5 Cu and 0.5 Fe, with traces of lead, agreeing approximately with the formula $\text{Cu}_2\text{S}, 2\text{Sb}_2\text{S}_3$. Before the blowpipe in the reducing flame, it gives off abundance of white fumes; when heated with sodium carbonate, it yields a bead of copper. Sp. gr. 5.03; hardness 3.5. In chemical composition it is most nearly related to wolfsbergite. According to Friedel, guejarite forms rhombic crystals, exhibiting the faces ∞P , ∞P^2 , $\infty P^{\frac{3}{2}}$, $\infty P^{\frac{5}{2}}$, with other faces subordinate. The habit of the crystals is flat prismatic; axial ratio 0.8220 : 1 : 0.7841. Angle $\infty P : \infty P = 101^\circ 9' 12''$, which is nearly the same as that of wolfsbergite.

H. W.

Examination of Livingstonite from a New Mexican Locality. By W. T. PAGE (*Chem. News*, **42**, 195).—The original locality where livingstonite was found is Huitzucó. The author, however, analysed a mineral from Guadalcázar in S. Luis, Potosi. The former occurs in small but pretty well-defined prisms, either single or grouped, together with general parallelism of direction, while the latter is found in small globular masses made up of delicate capillary or needle-like crystals interlaced with each other in all directions. Its colour is lead-grey with metallic lustre; streak cochineal-red; hardness = 2, brittle; sp. gr. = 4.41. Very easily fusible before the blowpipe flame, giving off copious white antimonial fumes. When it is heated in a glass tube with soda, globules of mercury are formed. Occurs in a gangue of gypsum along with native sulphur, but there is also some siliceous matter present. Obtained:—

S (combined).	S (free).	Sb.	Hg.	Fe.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.	SiO_2 .
15.12	3.67	32.22	13.95	0.42	15.54	18.01

Throwing out the iron and other non-essential substances, these figures give the atomic ratio—S : Sb : Hg = 7.04 : 4.0 : 1.04, obviously corresponding with the formula already established for livingstonite— $\text{HgS} \cdot 2\text{Sb}_2\text{S}_3$.

D. B.

Examination of an altered Livingstonite from Guadalcázar, S. Luis, Potosi, Mexico. By W. T. PAGE (*Chem. News*, **42**, 195).—This mineral formed a nearly compact mass, with traces only of crystalline structure, of iron-grey, almost black colour, very dark grey streak, and dull sub-metallic lustre. Hardness = 3; sp. gr. = 4.06. Analysis gave—

S (combined).	S (free).	Sb.	Hg.	O.
9.35	10.11	38.23	18.24	4.99.
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$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.	Fe.	Al_2O_3 .	Insoluble siliceous residue.
5.12	0.01	1.57	11.01

Neglecting non-essential ingredients, we obtain the atomic ratio, as compared with that of livingstonite—

$$\text{S} : \text{O} : \text{Sb} : \text{Hg} = 12.84 : 13.71 : 14.0 : 4.01$$

$$\text{S} : \text{Sb} : \text{Hg} = 28.00 : 16.0 : 4.00 \text{ (in livingstonite),}$$

No probable formula can be obtained. The substance in question seems to represent the result of chemical alteration of livingstonite by the replacement of more than half the sulphur by oxygen, forming probably Sb_2O_3 , and the removal of a further portion of the sulphur and a part of the antimony altogether.

D. B.

Artificial Production of Livingstonite. By A. L. BAKER (*Chem. News*, 42, 196).—The author succeeded in preparing livingstonite artificially by fusing together the sulphides of antimony and mercury, that of the latter somewhat in excess, in a stout glass tube filled with carbonic acid and sealed. The tube was kept in a vertical position, and the temperature of fusion maintained for some time, and after cooling the upper part of the fused mass was removed, leaving at the bottom an impure portion, in which the surplus mercuric sulphide had settled in consequence of its greater density. Another method consisted in fusing the mixed sulphides in an open crucible, in the upper part of which an atmosphere of carbonic acid was maintained, lowering the temperature gradually, and dropping in now and then a compact lump of artificially sublimed cinnabar until the mass was on the point of solidifying. The upper portion of the cooled mass was alone taken for examination. The product from each of these processes agreed essentially with the natural mineral in physical characters and chemical composition.

D. B.

Discovery of Antimony Oxide in Extensive Lodes at Sonora, Mexico. By E. T. Cox (*Sill. Jour.* [3], 20, 421).—The rocks in the immediate vicinity of these mines are quartzite and crystalline limestone. The oxide of antimony occurs in fissures from 2 to 20 feet wide; it has been found to a depth of 30 feet, and may be deeper. The ore varies in colour from almost white to dark brown. The sp. gr. of the purest specimens is 5.07, and they contain 75 per cent. of antimony. The entire lode probably averages 50 per cent. of metallic antimony.

C. W. W.

Antimonious Acid in a Vesuvian Product. By G. FREDA (*Jahrb. f. Min.*, 1881, 1, Ref. 198).—White deposits collected by Guiscardi in 1854 from the surface of a Vesuvian scoria gave by analysis—

Sb₂O₃. As₂O₃. F. SiO₂. CaO. MgO. Fe₂O₃. Na₂O. K₂O. SO₃. H₂O.
 0·94 18·54 28·55 17·88 7·60 4·12 1·66 11·38 8·52 1·16 10·22 = 110·57
 Deducting F equiv. to O 12·02

98·55

H. W.

The Kinzigites of Calabria. By DOM. LOVISATO (*Jahrb. f. Min.*, 1880, 2, Ref. 343).—The crystalline rocks of Calabria exhibit great variety of character, and are analogous in many respects to those of the Alps. Garnet in the forms ∞O and $3O3$. ∞O is a very important constituent of these rocks, chiefly of the southern and western declivities of the Sila. It is especially abundant in kinzigite, in which it occurs in regular garnet icositetrahedrons, having a diameter of 14 mm. or more. Kinzigite occurs very abundantly in Calabria Citeriore, forming thick strata above the gneiss, sometimes alternating with diorite and allied rocks, and exhibiting indications of transformation into gneiss and mica-slate. The dark micaceous constituents prevail in some parts, the light-coloured constituents, trichite feldspar and garnet in others, the prevalence of one or the other determining the more or less stratified character of the rock; some, which contain neither chromium nor manganese, have the red colour of the ruby or of pyrope; some kinzigites contain pinite, and many varieties are much decomposed.

The mineral species found by Lovisato in Calabria are the following:—Graphite, sulphur, rock-salt, fluorspar, zinc-blende, pyrites, marcasite, arsenical pyrites, cinnabar, copper pyrites, red ochre, menaccanite, limonite, quartz (including flint and jasper), opal, pyrolusite, spinell, magnetite, calcite (including marble), azurite, malachite, heavy spar, gypsum (in all varieties), ferrous sulphate; of silicates: disthene, sillimanite, tourmalin, epidote, idocrase, prehnite, garnet, mica, sericite, chlorite, serpentine (including chrysotil), kaolin (including clays), pinitoid, augite (including diallage, smaragdite), amphibole (including asbestos), talc, analcime, orthoclase, albite, oligoclase, labradorite (including gabbro), titanite;—Anthracite, lignite.

The spinell occurs in the granular limestone of Tiriolo, in azure-blue octohedrons, sometimes with ∞O , sometimes associated with idocrase and garnet. Between Catanzaro and the Tiriolo Mountain there stretches over two kinds of diorite a stratum of limestone, consisting of calcite, idocrase, and garnet, associated with blue spinell in splendid crystals, also epidote, pyrite, chalcopyrite, and blende. An analysis of the spinell gave—

Al ₂ O ₃ .	ZnO.	MgO.	FeO.	Sb ₂ O ₃ .
63·64	21·28	12·34	4·53	0·35 = 102·14

Neglecting the antimony oxide as an impurity, this analysis leads to the formula (Zn,Mg,Fe)Al₂O₄. These spinells, like the garnets above described, are more distinctly developed in proportion as they are smaller. Hardness = 7·5—8. Another clove-brown mineral, resembling spinell, was found in a white limestone below Maglie, but not in sufficient abundance for quantitative analysis.

H. W.

Conversion of the Distillation-vessels of Zinc-furnaces into Zinc-spinell and Tridymite. By H. SCHULZE and A. STEINER (*Jahrb. f. Min.*, 1881, 1, Mem. 120—160).—The muffles in which zinc oxide is heated with coke or charcoal for the preparation of metallic zinc are made of a mixture of 1 part raw clay and 2 parts burnt clay (chamotte). They last for about six weeks, during which time their mass undergoes two remarkable alterations, acquiring a coarsely columnar structure and a blue colour. The first of these alterations is shown by the fact that the disused muffles, when broken with a hammer, split up very easily at right angles to their surface, but offer great resistance to fracture in all other directions. This alteration of structure, doubtless the result of long-continued heating, is analogous to the columnar separation often observed in the hearths of blast-furnaces, and in sandstones which have been traversed by veins of basalt.

The blue coloration, which is deepest on the sides of the muffles and in the part above the charge, is due to the action of the zinc-vapours on the substance of the muffle. The distillation of the zinc begins at a temperature above 1200° C., and the greater part of the vapour passes over into receivers attached to the muffles, where it is condensed. A certain quantity, however, penetrates the porous substance of the muffle, partly stagnating and partly circulating in its pores, and finally passes out into the interior of the furnace, as shown by the fact that muffles which are not glazed on the outside often become covered with enamel-like crusts of a silicate rich in zinc, and sometimes with crystals of zinc oxide formed by the action of oxidising furnace-gases on the zinc-vapour.

The substance of the muffle thus altered appears, on examination with the microscope in thin sections, to consist of three compounds, viz., a glassy basis or ground-mass, interspersed with numerous granules and octohedrons of zinc aluminate or zinc-spinell, and crystals and crystalline groups of tridymite.

The glass is colourless, yellowish-brown or violet-brown, and mostly very homogeneous, only rarely exhibiting groups of microlites or dark-coloured minute granules, possibly products of devitrification. It appears to consist of an iron zinc silicate containing small quantities of alkalis and alkaline earth.

A blue fragment of a Freiberg muffle gave 88.8 per cent. matter insoluble in hydrochloric acid, and 11.2 per cent. decomposable by that acid, this latter portion consisting of a silicate containing 5.63 ZnO, 3.09 FeO, and 2.22 SiO₂ (total 11.01), with traces of lime, magnesia, and alkalis. The deep blue much altered mass of the Bensberg muffles yields only 0.5 per cent. soluble in hydrochloric acid.

Zinc-spinell. The dark-blue portions of the altered muffles consist for the most part of microcrystalline aggregates of roundish granules, appearing blue by transmitted light, and of small transparent and colourless crystals. Glass in these portions takes only a subordinate place, chiefly as filling-material of small cavities. Here and there, however, it occurs more abundantly, and in proportion as it breaks up the thick mass of the crystalline elements, the blue granules acquire more regular forms, and ultimately develop into very beautiful

octohedrons, the largest of which have an axial length of 0.33 to 0.06 mm. Most of these octohedrons are perfectly regular and sharp-edged, and here and there they unite to form twins. They are perfectly isotropic. The smallest and apparently most recently formed crystals are colourless, whereas the largest grains and crystals are blue. They are not attacked by hydrofluoric acid, so that this acid may be used for separating them from the accompanying glass. The best way of obtaining the substance of the octohedral crystals free for analysis is to treat them alternately with hydrofluoric and sulphuric acid till the residue no longer gives up any bases to sulphuric acid, and is free from gritty quartz-granules.

Analysis of the matter thus purified gave the following results:—

	Freiberg.	Bensberg.	Calculated for $\text{ZnO}, \text{Al}_2\text{O}_3$.
ZnO	42.60	43.74	44.07
FeO	1.12	0.73	—
Al_2O_3	55.61	55.43	55.93
	<hr/> 99.33	<hr/> 99.90	<hr/> 100

Consequently the octohedral crystals and crystalline granules consist of zinc aluminate or zinc-spinell having a small portion of the zinc oxide replaced by ferrous oxide.

The deep-blue muffles of Freiberg contain from 24.02 to 33.52 per cent. of this zinc-spinell; those of Bensberg from 29.77 to 32.58 per cent.

The cause of the blue coloration of the zinc-spinell crystals has not yet been satisfactorily determined. The pure spinell powder obtained by treating the crude substance of the muffles with hydrofluoric acid as above described, is not altered in colour by heating it in hydrogen or carbonic anhydride, or in chlorine, or in nascent oxygen evolved from potassium chlorate; but when this same powder is strongly ignited in contact with the air, it acquires a permanent light grey colour, which is not altered by heating in hydrogen or other reducing gas. This fact of the formation of a highly coloured substance at a white heat, and the subsequent decoloration by heating it in the air to a much lower temperature, is very remarkable, and has an important bearing on certain geological questions, inasmuch as it shows that the results of experiments made on isolated mineral substances do not afford any grounds for drawing conclusions as to the temperature or other conditions of the medium in which the minerals in question have been formed.

The specific gravity (at 14°) of blue crystals of zinc-spinell from Freiberg was found to be 4.52; from Bensberg, 4.49; of Bensberg crystals decolorised by heating, 4.45. The specific gravity of natural gahnite varies from 4.2 to 4.6.

The formation of the zinc-spinell is supposed by the authors to take place in the time which elapses between the daily renewal of the furnace-charge and the beginning of the distillation. During this interval water-vapour and carbonic anhydride are given off, and coming in contact with the zinc vapour in the pores of the muffle, give up oxygen

to the metal, and convert it into oxide; for although zinc oxide is reduced by carbonic oxide at a white heat, the metallic zinc may, at a lower temperature, such as prevails during the interval just mentioned, be reoxidised by the resulting carbonic anhydride (Kerl, *Grundriss der Metallhüttenkunde*, 342). Lastly, the zinc oxide thus formed acts upon the aluminium silicate of the muffle in such a manner as to form zinc-spinell and free silica: $\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{ZnO} = \text{ZnO}, \text{Al}_2\text{O}_3 + \text{SiO}_2$.

Tridymite.—The silica set free in the reaction just mentioned takes the form of small, transparent, colourless, double-refracting crystals, which exhibit the characters of native tridymite, such as occurs in the trachyte of Endöbenye and of the calcali-tufa of Pomasqui in Ecuador: it further resembles native tridymite in its solubility in a concentrated solution of sodium carbonate. Another portion of tridymite is produced by molecular alteration of quartz-granules in the original substance of the muffle, consequent on prolonged exposure to heat.

The blue substance of the muffles also contains a zinc silicate analogous to willemite, and a small proportion of bases not in combination with silica. The analysis of blue muffle-fragments from Bensberg yielded the following results:—

Zinc-spinell	32.58	
Silica	62.82	
Alumina	0.83	} Bases soluble in hydro- fluoric acid.
Ferric oxide	1.62	
Zinc oxide	1.30	
Alkalis and alkaline earths.	0.85	

100

The changes in the zinc-muffles above described have an important bearing on many geological phenomena. Thus various members of the spinell group—as magnetite, franklinite, gahnite, pleonast, and magnesia-spinell, are often found in limestones which have been intersected by eruptive rocks, or as fragments enclosed and metamorphosed by the latter; also in limestones of ancient date, which from their structure and the minerals contained in them, have evidently been at some time or other in a state similar to that of the metamorphic limestones above mentioned. Now the formation of these minerals was formerly regarded as a proof that the limestones in which they occur must have been for some time in the fused state; but the above-described changes in the zinc-muffles clearly show that the assumption of such a state of fusion is by no means necessary, and that the minerals in question may have been formed in the solid limestone, if it were exposed to the action of heat, and at the same time penetrated by gases and vapours of suitable composition. Another argument in favour of the view just mentioned is afforded by the diopsides, which have been formed in somewhat considerable quantity at the Blaenavon Iron Works, in Wales, these diopsides having been found in bricks prepared from a limestone containing clay and magnesia, and exposed to intense and prolonged heat in contact with

the quartziferous walls of a furnace. Lastly, the changes in the zinc-muffles may be compared with those which sometimes take place in the fissures of fumeroles and the cavities of volcanic bombs, resulting in the formation of minerals which may be regarded as products of sublimation. Silicates thus formed were described by Scacchi in 1852, as lining the walls of a volcanic bocca on Vesuvius; and G. vom Rath, a few years later, described angites found, together with iron-glance, in a fumerole-cleft of the Eiterkopf, near Plaidt, the formation of which could not be explained otherwise than by sublimation. But the most abundant of the mineral formations in question was furnished by the Vesuvian eruption of 1872, in which bombs of ancient leucitophyr, and others made up of cemented fragments of this rock, were thrown out and fell into the flowing lava. In the pores of these rocks and the intervals between the fragments, Scacchi discovered nests of leucite, sanidin, augite, garnet, nephelin, microsommite, sodalite, hornblende, mica, iron-glance, magnetite, and apatite, and Heim afterwards found spinell. G. vom Rath agrees with Scacchi and Heim in regarding these minerals as new formations, produced either in the depths of the mountain or within the lava current, but in either case by the effect of renewed volcanic activity on the ancient leucitophyr. He further points out that the ejected blocks must have been penetrated by a mineral-forming Aura, probably consisting of the vapours of water and sodium chloride, and he regards these vapours, which are abundantly produced in volcanic eruptions, as the originators and propagators of the most important among the processes here under consideration. This view is undoubtedly corroborated by the study of the above-described changes observed in zinc-muffles. In the one case as in the other, the action of gases on a softened mass has given rise to molecular transformations and sublimation, resulting in the production of a variety of minerals.

H. W.

Materials for the Mineralogy of Russia. (Vol. 7, pp. 177—384, and Vol. 8, pp. 1—32). By N. VON KOKSCHAROW (*Jahrb. f. Min.*, 1879, 892—895).—The seventh volume contains results of the examinations of mica, “waluewite,” breunnerite, and iron pyrites, also small notices on mica, dolomite, zircon, titanite iron, chrysolite, sodalite, aragonite, diopside, perowskite, and skorodite. The eighth volume contains the new works of Tschermak and Bauer on the micas, and also remarks by Des Cloizeaux. *Breunnerite*: The terminal angle on the primary rhombohedron was found to be $107^{\circ} 23' 40''$, which is the mean of all previous determinations. The following forms have not been observed before: $-\frac{1}{4}R$; $3R$; $4R$; $6R$; $7R$; $-\frac{1}{2}R$; $-2R$; $-5R$; and $-8R$. It occurs in many localities. Some brown crystals from the chlorite beds of Miask and having R (term.) = $107^{\circ} 24'$ gave on analysis:—

CO ₂ .	MgO.	FeO.	Fe ₂ O ₃ .
49.97	40.50	8.55	0.67 = 99.69

Sp. gr. 3.10.

Iron Pyrites.—This is very widely spread, and very fine crystals occur. The following forms have been observed: O ; $\infty O\infty$; ∞O ;

202; $\left[\frac{\infty 02}{2}\right]$; $\left[\frac{\infty 0\frac{2}{3}}{2}\right]$; $\left[\frac{\infty 03}{2}\right]$; $\left[\frac{402}{2}\right]$; $\left[\frac{\frac{9}{2} 0\frac{3}{2}}{2}\right]$; the latter being a new form.

Mica.—Tschermak's results do not differ essentially from those of v. Kokscharow, but he does not consider the monosymmetrical character to be proved, for the variation of the acute bisectrix from the normal on the basal plane is exceedingly small, and moreover is not constant in its direction. The crystallographical and optical results of Bauer are in accordance with those of Tschermak. H. B.

Analysis of Native Sodium Sulphate from Sicily. By E. PATERNÒ (*R. Accad. dei Lincei*, 1879–80 [3], 4, 22; *Jahrb. f. Min.*, 1881, 1, Ref. 199).—Glauber's salt was discovered several years ago in the commune of Monte Doro in Sicily, and recently a bed about two meters thick has begun to be worked. The salt consists of a thick mass, perfectly transparent and colourless when fresh, but quickly efflorescing, and mixed with a small quantity of clay. The proportion of water in two samples was found to be 55·68 per cent., and of SO₃ in the anhydrous salt, 56·15 and 56·25 per cent., pure Glauber's salt, Na₂SO₄ + 10H₂O, requiring 55·90 per cent. water, and the anhydrous salt 56·33 per cent. SO₃. The crude salt contains in addition only traces of lime and magnesia, so that it is remarkably pure.

H. W.

Celestine from the Muschelkalk of Jühnde, near Gottingen. By S. M. BABCOCK (*Jahrb. f. Min.*, 1879, 835–838).—The crystals, attaining a length of 1 cm., are interesting on account of the predominance of the faces $\frac{1}{2}P\infty$ and $P\infty$, whilst P, ∞P , and 0P are quite secondary. Only some few were fit for accurate measurement, giving: $\frac{1}{2}P\infty$ (over 0P) = 78° 49' 30"; $P\infty$: 0P = 127° 58' 24". Cleavage: ∞P and 0P. The analysis gave—

Sr.	Ca.	SO ₄ .	Insoluble.
47·45	0·17	51·82	0·22 = 99·66

The optical axes lay parallel $\infty P\infty$, with the brachy-axis as acute bisectrix; the mean refractive index and the optical axial angle were found to agree with Arzruni's measurements. H. B.

Herrengrundite, a New Basic Copper Sulphate. By A. BREZINA (*Jahrb. f. Min.*, 1879, 897–900).—After deducting the lime, 2·03 per cent., and the corresponding quantities of water and sulphuric acid necessary to form gypsum, its composition was found to be—

SO ₃ .	CuO.	H ₂ O.
23·04	57·52	19·44 = 100·00

Colour, deep emerald-green. H. = 2·5. Small hexagonal plates of the monoclinic system, tabular through 0P and parallel to which they have a perfect cleavage. 0P is striated parallel to the ortho-axis; the angles are somewhat varying; $a : b : c = 1·8161 : 1 : 2·8004$ and $\beta = 88° 50·2'$. Forms observed 0P, a series of prisms apparently ∞P . $\infty P\frac{9}{8}$. $\infty P\frac{5}{4}$. $\infty P\frac{5}{3}$. $\infty P\frac{5}{2}$. $\infty P2$. $\infty P\frac{5}{2}$; also $\pm \frac{5}{2}P\infty$. $\pm P\infty$. + P. The plane of the optic axes is almost perpendicular to 0P, and

parallel to the striation on this face; optical character negative, dispersion $\rho < \nu$; the optic axial angle measured in air is for Li = $59^\circ 1'6''$, Na = $66^\circ 6'$, Tl = $68^\circ 39'$; it is dichroic, vibrations parallel, ϵ = yellowish-green, parallel η = bluish-green. The author compares this mineral with langite, brochantite, and atacamite.

H. B.

Canadian Apatite. By C. HOFFMANN (*Chemical Contributions to the Geology of Canada*, Montreal, 1880).—This paper contains descriptions and analyses of eight varieties of apatite, all containing fluorine, occurring in large quantities in various parts of the Dominion of Canada. The proportion of phosphoric acid in these apatites ranges from 34.03 to 41.08 per cent. P_2O_5 , equivalent to 74.29 to 89.68 per cent. $Ca_3P_2O_8$, and that of fluorine from 2.855 to 3.863 per cent. The large proportion of calcium phosphate renders them well adapted for the manufacture of superphosphate.

H. W.

Two New Minerals from the Eleonora Mine in the Dünsberg near Giessen. By A. NIES (*Jahrb. f. Min.*, 1881, 1, Ref. 16).—1. Eleonorite, $2(Fe_2)^{vi}P_2O_8 \cdot H_6(Fe_2)^{vi}O_6 + 15H_2O$. This mineral occurs, together with strengite, in an isolated block of brown hæmatite. It was at first regarded as monoclinic, but is now described by the author as orthorhombic, although some of its optical characters do not quite agree with that system. Cleavage parallel to the (undetermined) dome-faces and the lateral pinacoid. $H. = 3$. Sp. gr. = 2.40. In the fresh state it is translucent, and has a glassy lustre and a dark brown colour, often with variegated tarnish. Streak yellow. Soluble in hydrochloric and in warm nitric acids.

2. Picite (named from *Picites resinaceus*).—Composition $4(Fe)^{vi}P_2O_8 \cdot 3H_6(Fe_2)^{vi}O_6 + 27H_2O$. Amorphous: occurs in thin coatings or small stalactitic and globular forms. Fracture conchoidal. $H. = 3-4$. Sp. gr. = 2.83. Lustre vitreous to fatty. Translucent, dark-brown, often with variegated tarnish. Streak yellow. The author regards picite as probably identical with the mineral described by Boricky from the Hrbek mine near St. Benigna.

H. W.

The Phosphates of Waldgirmes. By A. STRENG (*Jahrb. f. Min.*, 1881, 1, Mem. 101—119).—These phosphates are found in the "Rothläufchen" iron mine near Waldgirmes, a village situated between Wetzlar and Giessen. The brown iron ore of this mine, at least in its upper parts, is traversed by numerous clefts which are partly or wholly filled with crystals of eleonorite, cacoxene, kraurite, strengite, and wavellite; perfectly compact and apparently amorphous ferric phosphate (picite) is likewise present. These phosphates occur in the clefts either singly or in groups. The clefts are parallel, and often lie close together, so that the iron ore is easily split into thin scales, and it is in this thin scaly brown iron ore that the finest crystals of the above-mentioned phosphates are found.

1. *Eleonorite*.—This mineral, discovered by Nies in the Eleonora mine near Giessen, and regarded by him as rhombic, belongs, according to Streng—whose investigations were made upon much better-defined crystals—to the monoclinic system. Axes $a : b : c =$

2.755:1:4.0157; $\beta = 48^\circ 33'$. Observed faces: $+P$, $\infty P\infty$, $0P$, with a negative hemiorthodome very subordinate. The face $\infty P\infty$ is striated parallel to its combination-edge with $0P$, in consequence of the alternating combination of the two faces. The microscope further reveals a very fine striation parallel to the combination-edge with P , indicating a polysynthetic twin-combination. The crystals are mostly tabular parallel to $\infty P\infty$, and prismatically elongated in the direction of the orthodiagonal; in their development they somewhat resemble epidote and trona, but most strikingly the crystals of lazulite from Lincoln County, Georgia, which are flattened parallel to a pyramidal face. The crystals are only 1—2 mm. in size, and are commonly united in druses. Cleavage parallel to the orthopinacoid. Hardness = 3—4; sp. gr. not determined.* Colour red-brown to dark hyacinth-red. Streak yellow. The crystals, viewed under the microscope with a Nicol's prism, appear strongly dichroic, the rays which vibrate parallel to the orthodiagonal having a light yellow colour, while those which vibrate at right angles to this axis are dark red-brown. The positions of extinction are also parallel and perpendicular to this axis. In other positions, with crossed Nicols, brilliant interference-colours are observed. Lustre on the orthopinacoidal face bright glassy, inclining to nacreous. The crystals, when examined by the microscope, appear very pure and free from enclosed minerals. Before the blow-pipe, eleonorite melts easily to a black globule, which has a metallic lustre, and solidifies in the crystalline state. It dissolves readily in hydrochloric acid.

Crystallised eleonorite gave by analysis 31.88 per cent. P_2O_5 , 51.94 Fe_2O_3 , and 16.37 H_2O ; a specimen in the form of a radio-laminated crust on brown hæmatite, gave 31.78 P_2O_5 , 52.05 Fe_2O_3 , and 16.56 H_2O . These analyses, especially the first, agree nearly with the formula $Fe_5P_4O_{19} + 8H_2O$, or $2(Fe_2O_3, P_2O_5) + Fe_2O_3, 3H_2O + 5H_2O$, which requires 31.58 per cent. P_2O_5 , 52.63 Fe_2O_3 , and 15.79 H_2O . This composition approximates nearly to that of beraunite from St. Benigna in Bohemia, and from the Father Abraham mine at Scheibenberg in Saxony (this Journal, 1873, 851); the two minerals are also much alike in their physical characters, but the resemblance is not perhaps quite close enough to establish their identity.

2. *Cacoxene*.—It has already been mentioned that Nies regarded the brown radio-fibrous spherical masses from the Eleonora mine as *eleonorite*, assigning to them the formula $2(Fe_2O_3, P_2O_5) + Fe_2O_3, 3H_2O + 15H_2O$, which is very nearly related to that of *cacoxene*. The same mineral is found associated with *cacoxene* in the Rotläufchen mine. The analyses hitherto made of *cacoxene* differ considerably from one another, as the following comparison will show:—

	Steinman.	Richardson.	v. Hauer.
P_2O_5	22.28	21.85	19.63
Fe_2O_3	45.32	45.94	47.64
H_2O	32.28	32.19	32.72

* According to Streng, the statements of Nies respecting the sp. gr. of eleonorite, really apply to the radio-fibrous spherules by which that mineral was accompanied.

The analysis of the brown mineral from the Eleonora mine differs from all these in giving a much larger proportion of phosphoric acid, viz., 26.18 per cent. P_2O_5 . On the other hand it stands much nearer to the dingy-green, kidney-shaped, wavelitic mineral mentioned by v. Hauer as occurring together with cacoxene, at St. Benigna. This green mineral, which does not resemble cacoxene in its physical properties, gave, as a mean of two analyses, 25.71 per cent. P_2O_5 , 41.46 Fe_2O_3 , and 32.81 H_2O . The yellow cacoxene occurring in twisted fibrous groups at the Eleonora and Rothläufchen mines has the same composition as the brown mineral analysed by Nies, whence it appears that the two minerals are identical, and differ only in their mode of aggregation, the brown mineral forming compact radio-fibrous spherules. It is true that the brown radio-fibrous groups are distinctly dichroic, whereas the yellow needles are apparently not so; but these latter likewise exhibit dichroism when a considerable number of them are laid parallel to each other.

Boricky (*Wien. Akad. Ber.*, 1867, 56, 17) states that dufrenite, which partly forms the raw material for the production of beraunite, likewise yields the material for the formation of a brown amorphous phosphate, and is convertible into cacoxene: he was able to trace the conversion of dufrenite into cacoxene in all its stages. The transformation is not perceptible either at the Eleonora or at the Rothläufchen mine. On the other hand a transition may sometimes be observed of the brown radio-fibrous spherules into the brown amorphous phosphate (picite according to Nies), under circumstances which leave it doubtful which of the two is the original mineral.

3. *Kraurite*.—This mineral occurs together with eleonorite, and sometimes intergrown therewith, in rhombic crystals, usually of a dark-green or nearly black colour. They are from 1 to 2 mm. long, and generally united in parallel or nearly parallel groups. The simplest and best defined crystals exhibit the combination $\infty P\infty . \infty P\infty . P\infty$; others the combination $\infty P\infty . \infty P . P\infty$. Crystals of the first kind also occur, having the combination-edge of $\infty P\infty$ and $\infty P\infty$ truncated by ∞P . The face $\infty P\infty$ also occurs subordinate. ∞P and $\infty P\infty$ have a strong lustre: the face $\infty P\infty$ is also vertically striated; $\infty P\infty$ is more deeply striated, and consequently less lustrous. The faces $P\infty$ are always much rounded, so that the two run into one another without forming an edge; they are also for the most part less brilliant than the rest, or quite dull. Angle $\infty P : \infty P = 97^\circ 44'$. $P\infty : P\infty = 133^\circ 50'$. Axes $a : b : c$ approximately = 0.8734 : 1 : 0.426. The crystals appear to cleave only parallel to $\infty P\infty$. Colour by reflected light dark-green to black in comparatively thick pieces, dark red-brown in thinner ones; by transmitted light dark brown with a tinge of green in thick, yellow in thin laminae. The mineral is also strongly dichroic.

The kraurite of Rothläufchen is translucent only in very thin splinters. It has a metallic vitreous to porcelain-like lustre. Fracture uneven. Streak brownish-yellow. Brittle. Hardness greater than 4. Sp. gr. = 3.39. Under the microscope it appears nearly free from foreign enclosures. It dissolves easily in hydrochloric, less easily in dilute sulphuric acid. Melts before the blowpipe to a black metal.

lically lustrous bead, which on the fractured surface appears dark-brown, crystalline, fine-grained, and blistered.

Analysis gave 31.82 per cent. P_2O_5 , 60.20 Fe_2O_3 , 1.53 FeO , and 8.03 H_2O , leading to the formula $3Fe'''_2P_2O_8 + 2Fe'''_2H_6O_6$. The mineral is therefore a ferric phosphate, having, with exception of the small quantity of ferrous oxide, the same composition as the kraurite of the Hollerterzug near Siegen.

Very remarkable is the intergrowth with this mineral of dark red-brown slender monoclinic needles, which the author first supposed to consist of eleonorite, but now regards as another form of kraurite formed subsequently to the brownish-green crystals above described; the crystals of the two forms agree in their optical characters, and approximately in the magnitudes of their corresponding angles. The author therefore concludes that the crystals of kraurite above described as rhombic, are really monoclinic, and that their rhombic form is due to a twin-formation according to the orthopinacoid.

4. *Picite*.—This mineral, called by Breithaupt *Picites resinaceus*, has been correctly described and analysed by Nies (p. 525). It occurs in the Rothläufchen as well as in the Eleonora mine.

5. *Strengite*.—Occurs somewhat rarely in the Rothläufchen mine, together with eleonorite, in small, colourless, often very well-defined crystals, having exactly the same development as those in the Eleonora mine.

6. *Wavellite*.—This mineral, which is found on the summit of the Diensberg, in radio-fibrous masses on clefts of the siliceous slate which forms the declivity of the Eleonora mine, occurs also in a similar manner on the declivity of the Rothläufchen mine, being found in that part of the mine which is rich in phosphates, in numerous, very small but distinct crystals, exhibiting a large number of faces. On account of their minuteness, the only way of seeing all their faces is to view them under the microscope with a low power, and by reflected light. They are prismatically elongated in the direction of the principal axes. The prism with an angle of about 125° is almost the only form that can be recognised in the zone of the principal axis, the face $\infty P\infty$ occurring also very subordinate. The crystals are perfectly colourless and transparent, with a bright glassy lustre. They gave by analysis 24.48 per cent. H_2O and 34.94 P_2O_5 , agreeing perfectly with other analyses of wavellite. With regard to their optical properties, the position of extinction coincides exactly with the principal axis. Wavellite is therefore undoubtedly rhombic.

Besides the phosphates above mentioned, there are also found small radio-fibrous concentrically scaly spherules, which have a light-grey colour, dissolve for the most part in hydrochloric acid, and, when heated before the blowpipe, turn dark brown without melting, but split up into a number of concentric scales. The author is of opinion that this mineral may be regarded as a barandite rich in alumina, or perhaps as a ferruginous wavellite.

The following table exhibits the molecular proportions of the phosphates above described:—



Kraurite from—

St. Benigna, I	= 2 : 3·6	: 5	or 1·7	: 3	: 4·1
„ II	= 2 : 3·2	: 4·5	„ 1·87	: 3	: 4·1

Kraurite from—

Rothläufchen	= 2 : 3·35	: 4	„ 1·78	: 3	: 3·5
Beraunite (Tschermak)	= 2 : 3·2	: 7·2	„ 1·87	: 3	: 6·8
„ (Boricky) I.	= 2 : 3·5	: 7·9	„ 1·8	: 3	: 7·2
„ II.	= 2 : 3·4	: 7·8	„ 1·7	: 3	: 6·9
(Frenzel)	= 2 : 3·4	: 9·1	„ 1·8	: 3	: 8
Eleonorite	= 2 : 3	: 8			
Strengite	= 2 : 4	: 8			
Cacoxene (Nies)	= 2 : 3	: 18·5			
Cacoxene ? (v. Hauer) ..	= 2 : 2·9	: 20	„ 2·1	: 3	: 21
Cacoxene (Steinmann).	= 2 : 3·6	: 22·9	„ 1·66	: 3	: 19·1
Cacoxene (Richardson)	= 2 : 3·7	: 23·2	„ 1·61	: 3	: 18·7
Cacoxene (v. Hauer) ..	= 2 : 4·3	: 26·3	„ 1·39	: 3	: 18·3
Picite	= 2 : 3·5	: 18	„ 4	: 7	: 36

The mode of occurrence of all these phosphates in the Rothläufchen mine is very much like that of their occurrence at the Hrbeck mine near St. Benigna. H. W.

Composition of Dufrenite from Rockbridge Co., Virginia.

By F. A. MASSIE (*Chem. News*, 42, 181).—This mineral occurs in nodular masses of various sizes, showing well-marked radiated structure on being broken, the mass being made up of slender prisms closely compacted. Hardness = a little over 4; sp. gr. = 3·454; faint silky lustre; colour very dark blackish-green, almost black; streak greyish-green. Analysis gave—

Fe_2O_3 .	Al_2O_3 .	FeO .	MnO .	MgO .	P_2O_5 .	SiO_2 .	H_2O .
50·89	0·29	6·06	0·24	2·16	31·66	0·20	8·35

From these numbers, it is shown that this mineral corresponds pretty nearly with a mixture of normal dufrenite $\text{Fe}'''_2(\text{HO})_3\text{PO}_4$, and anhydrous ferrous pyrophosphate, $\text{Fe}''_2\text{P}_2\text{O}_7$, in about the ratio of 3 mols. of the latter to 4 of the former. D. B.

A New and Remarkable Mineral Locality in Fairfield, Connecticut, with a Description of New Species occurring there. Third Paper. By G. J. BRUSH and E. S. DANA (*Amer. J. Sci.*, 18, 45).—In this locality, as already observed (this Journal, 36, 891), phosphates of manganese occur together with feldspar (albite), and spodumene. The spodumene is mostly decomposed, and the products of its decomposition, chiefly cymatolite (pihlite), will form the subject of a future communication. Associated with it are also: manganese-spar, apatite, garnet, uranium pitch-blende in black shining octohedrons; also uranium phosphates and a silicate containing uranium, nearly related to chrysolite. Lastly, a green chloritic mineral is found in considerable quantity, together with a rather large

mass of ordinary dark-coloured lithiophilite occurring in roundish or angular lumps of the size of a cherry, or several inches in diameter, and cellular or granular manganese-spar containing crystals of chabazite in its cavities. This green mineral is intimately mixed with all the phosphates, especially with eosphorite.

The comparatively dark-coloured lithiophilite, of clove-brown colour, contains more manganese and less iron than the variety previously analysed (this Journal, **36**, 892). Its analysis gave:—

P ₂ O ₅ .	FeO.	MnO.	Li ₂ O.	Na ₂ O.	H ₂ O.	Gangue.
45.22	13.01	32.02	9.26	0.29	0.17	0.29 = 100.26

Hence the formula $R'R''PO_4 = R'_3PO_4, R''_3P_2O_8$.

A comparison of the analyses of triphylite from various localities collected by S. L. Penfield (this Journal, **36**, 695) with those of lithiophilite, shows that between these two minerals there exists a series similar to that formed by the carbonates of manganese and iron. This series extends from the triphylite of Bodenmais containing 36.21 per cent. FeO and 8.96 MnO to lithiophilite (first occurrence) containing 4.02 per cent. FeO and 40.86 MnO. The specific gravity of the darker-coloured lithiophilite is 3.482.

The eosphorite imbedded in the green chloritic mineral likewise differs somewhat in composition from the previously-analysed mineral (this Journal, **36**, 20), though the two exhibit similar properties.

P ₂ O ₅ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	H ₂ O.	Insol.
31.39	21.34	6.62	22.92	1.48	15.28	1.46 = 100.49

Hence the formula $R_2Al_2P_2O_{10} \cdot 4H_2O = Al_2P_2O_8 + 2H_2(Mn, Fe)O_2 + 2H_2O$. Sp. gr. = 3.11.

The green chloritic mineral above mentioned was found, on further examination, not to consist of a single compound, as even its purest portions exhibited under the microscope numerous small crystals of quartz and apatite, whilst felspar, mica, quartz, apatite, chabazite, and the phosphates of manganese were visible even by macroscopic examination. The granular to cryptocrystalline ground-mass thereby exhibited could not be further resolved by the microscope, and appeared to be tolerably homogeneous.

An analysis made with very pure material, gave:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	Na ₂ O.	K ₂ O.	Li ₂ O.	CaO.
20.72	14.67	2.67	19.56	2.22	5.19	0.51	0.09	traces	12.34
		P ₂ O ₅ .	Insol.	H ₂ O.					
		8.84	3.89	8.84					

Deducting the phosphoric acid, together with the quantity of lime required to form apatite therewith, and neglecting the insoluble residue, the composition of the chloritic mineral comes out as follows:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Na ₂ O.
27.43	19.42	3.54	25.89	2.94	6.87	0.95	0.68
		K ₂ O.	H ₂ O.				
		0.12	11.70				

11.70 = 99.54

a result which approximates very nearly to the composition of certain minerals of the chlorite group, viz., delessite and chlorite.

Heated in a closed tube, the mineral gives off water and melts to a black magnetic mass. With fluxes it exhibits the reactions of silica, iron, and manganese. It dissolves in hydrochloric acid, leaving a residue of silica and of an aluminium silicate (perhaps cymatolite). Hardness = 2·5. Sp. gr. of the purest portions = 2·85—2·89.

Chabasite is found imbedded in irregular masses in quartz, in the chloritic mineral, and in the cellular or granular manganese-spar. In the cavities of this latter it occurs also in small rhombohedrons, whose polar edge-angle measures $96^{\circ} 45'$. Analysis of material as pure as could be obtained gave:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Quartz.
49·32	17·58	1·99	0·56	6·73	2·83	1·44	17·83	2·78 = 100·96

Lustre vitreous to waxy; colour, dark-yellow to reddish-brown. H. = 4·5. Sp. gr. 2·16.

Rhodochrosite (Manganspath).—This mineral, differing from that formerly described, was found imbedded in lithiophilite, exhibiting a flesh-red colour, and differing from the latter only by its rhombohedral cleavage, the cleavage-faces being, however, dull-coloured or white. It was granular and much contaminated with quartz, apatite, and chabasite.

Analysis gave as a mean result:—

CO ₂ .	FeO.	MnO.	CaO.	MgO.	Insol.
37·80	16·76	44·59	0·33	traces	0·32 = 99·80

agreeing nearly with the formula MnO, CO_2 .

H. W.

Autunite. By A. BREZINA (*Jahrb. f. Min.*, 1879, 900—901).—Former work on this subject is reviewed by the author, who has obtained specimens from Johanngeorgenstadt, which he does not consider as rhombic, but monosymmetrical with the values $a : b : c = 0·3463 : 1 : 0·3525$ and $\beta = 89^{\circ} 30'$. Crystals tabular through $\infty \text{P} \infty$, and bordered by $\infty \text{P} \infty$ and 0P , or two small unmeasurable faces. The vibration directions in $\infty \text{P} \infty$ make $4^{\circ} 40'$ with the edge $\infty \text{P} \infty : \infty \text{P} \infty$. Twins very common with the twin plane $-\text{P} \infty$.

H. B.

Hedyphane containing Baryta, from Laangban. By G. LINDSTRÖM (*Jahrb. f. Min.*, 1879, 896).—Resembles ordinary hedyphane except in its higher sp. gr., viz., 5·82 instead of 5·4—5·5; and in containing barium:—

As ₂ O ₅ .	P ₂ O ₅ .	CO ₂ .	Cl.	PbO.	BaO.	CaO.	MgO.	FeO.	Na ₂ O.
28·18	0·53	1·07	3·05	49·44	8·03	8·99	0·24	0·08	0·15
			K ₂ O.	Insol.					
			0·09	0·42 = 100·27					

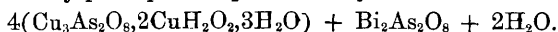
Leaving out the FeO, K₂O, Na₂O, CaCO₃, and “insoluble,” these numbers give the normal formula $3(3\text{RO}.\text{As}_2\text{O}_5) + \text{PbCl}_2$.

H. B.

Arsenates from Joachimsthal. By A. SCHRAUF (*Zeitschr. f. Krystallographie*, 1880, **4**, 277—285; *Jahrb. f. Min.*, 1881, **1**, 14).—1. Mixite, a new copper-bismuth hydroarsenate, was found, together with chalkolite and bismuthite, amongst decomposed bismuth ores. Colour emerald to bluish-green. Streak lighter. $H. = 3-4$. Sp. gr. = 2.66. Finest fibres nearly transparent. It occurs on impure yellow bismuth ochre, partly in films, partly in irregularly scattered thick portions. In dilute nitric acid it immediately becomes covered with a layer of shining white powder, consisting of insoluble bismuth arsenate, whilst the cupric arsenate present is completely dissolved. The mean of several analyses gave:—

CuO.	FeO.	CaO.	Bi ₂ O ₃ .	$\underbrace{\text{As}_2\text{O}_5, \text{P}_2\text{O}_5}_{\text{}}$	H ₂ O.
43.21	1.52	0.83	13.07	30.45	11.07 = 100.15

leading to the formula $\text{Cu}_{20}\text{Bi}_2\text{As}_{10}\text{H}_{44}\text{O}_{70}$, which requires 44.08 per cent. CuO, 12.99 Bi₂O₃, 31.93 As₂O₅, and 11.00 H₂O. In the exsiccator the mineral loses in 24 hours 1.84 per cent. water, which is reabsorbed on exposure to the air; at 100° it loses 4.09, and at 175°, 5.86 per cent. water. At a red heat the light colour changes to a permanent blackish-green. As the bismuth arsenate is very easily separable, the mineral may perhaps be represented by the formula



The minerals by whose decomposition mixite is produced, consist of various bismuth ores and bismuthiferous fahl-ores. The accompanying uranium-mica contains P₂O₅, and not As₂O₅, as might have been expected in a mineral associated with mixite. It is, in fact, chalkolite, and apparently optically uniaxial. Another accompanying mineral is bismuth-carbonate in prisms with conchoidal or curved faces, mostly hollow within, grey to brownish-green, with vitreous to adamantine lustre, decrepitating, containing Bi, CO₂, and H₂O, but no arsenic.

2. *Wapplerite*.—This mineral was formerly described by the author as monoclinic (this Journal, 1875, 739), but is now regarded by him as triclinic with the axial ratio $a : b : c = 1 : 1.11002 : 0.29037$, and the axial angles $\alpha = 90^\circ 13' 55''$; $\beta = 95^\circ 20'$; $\gamma = 90^\circ 10' 35''$, deviating therefore but slightly from a monoclinic system. The morphological relations of wapplerite to rösslerite formerly pointed out by the author, he now regards as established. Wapplerite is accordingly the original mineral from which rösslerite is formed by addition of water. Some crystals of wapplerite, which had been kept for two years in corked bottles, were found to be converted in their interior into a white incoherent mass.

Pharmacolite.—Besides the faces of this mineral given in *Miller's Mineralogy*, viz., $\infty P\infty$, ∞P , $\infty P\bar{3}$, $P\infty$, $3P\bar{3}$, the author has observed $+P$. The faces of this form are, however, very small. The axial system is $a : b : c = 0.61373 : 1 : 0.36223$; $\beta = 88^\circ 13' 4''$.

H. W.

Analyses of Minerals. By T. NORDSTRÖM (*Jahrb. f. Min.*, 1879, 895—896).—(1.) Vanadinite, discovered at Bølet, gave on analysis:—

Cl.	Pb.	PbO.	FeO.	V ₂ O ₅ by loss.
2.34	6.67	71.99	1.39	17.61 = 100.00

Phosphoric acid was absent. E. Cohen compares with the above an analysis made on a sample—form ∞ P.P.—from Wanlock Head.

SiO ₂ .	FeO.	CaO.	MgO.	Cl.	Pb.	PbO.	V ₂ O ₅ .	As ₂ O ₅ .
0.28	1.32	0.81	0.21	2.44	7.15	69.17	18.89	0.53 = 100.80

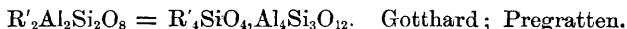
(2.) A mineral containing selenium from Fahlun. This, which does not appear to be a definite substance, contains approximately Bi 50 per cent., Pb 17—20 per cent., S and Se 5 per cent., a percentage greater than any previously met with in the district. H. B.

Chemical Composition of the Micas. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1881, 1, Ref. 365—371).—In this paper the author gives a chemical classification of the micas founded on his analyses of the lithia micas published in 1879 (this Journal, 35, 19) and sixteen new analyses of micas of different species. The general result of these investigations is, that micas are partly singulosilicates, $R_4SiO_4 = 2R_2O, SiO_2$, and partly compounds of these with bisilicates, or $R_2SiO_3 = R_2O, SiO_2$. Every mica is made up of similarly constituted silicates. These, however, are not present in constant molecular proportions, and consequently their union must be regarded as resulting not merely from the isomorphism of corresponding degrees of silicatisation of the metals R', R'', and $(R_2)^{vi}$, but also from that of the singulosilicates and bisilicates.

Micas which qualitatively are very closely related to one another are not always stoichiometrically analogous. Rammelsberg therefore groups the micas according to their qualitative resemblance, the alkali-micas (those containing only alkali-metals) being in this respect contrasted with those which also contain bivalent elements, viz., the magnesium, barium, and iron micas. This mode of classification implies that Rammelsberg does not accept Tschermak's classification of the micas founded on their physical as well as their chemical properties (this Journal, 38, 532). In opposition to this mode of arrangement, he points out that the physical, and especially the optical, differences of these minerals, cannot always be shown to arise from difference of chemical composition.

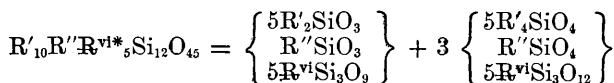
The following are the results of Rammelsberg's new analyses and the formulæ of the several groups thence deduced:—

I. ALKALI MICAS.—A. *Sodium-mica*.—Singulosilicates,



B. *Potassium Micas*.—First Division. — Singulosilicates, $R_2Al_2Si_2O_8$, almost always mixed with small quantities of Mg and Fe in the form R''_2SiO_4 . Leinsterberg; Glendalough, Dreifelsengebirge; Grindelwald.

Second Division.—Compounds of Singulo- and Bi-silicates.—*First Series*.—1 mol. bisilicate to 3 mols. singulosilicate.



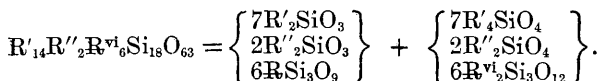
Newly analysed: (1.) South Royalston, Massachusetts; broadly laminar, grey. (2.) Ytterby; white. (3.) Braddbo, near Fahlun; brownish-grey.

	F.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	K ₂ O.	Na ₂ O.
(1.)	0.74	45.97	30.40	5.11	1.05	2.03	9.92	0.59
(2.)	0.94	45.21	33.40	2.78	2.00	1.58	10.71	0.42
(3.)	0.64	47.13	30.60	4.81	0.61	1.30	10.26	0.74

	H ₂ O†.	H ₂ O‡
(1.)	4.00	0.50 = 100.31
(2.)	3.95	0.33 = 100.32
(3.)	4.02	0.76 = 100.87

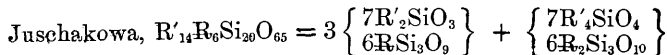
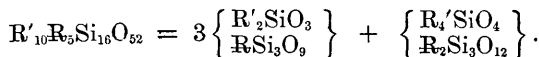
To this division also belong potassium-micas from Zillerthal, Rothenkopf, Aschaffenburg, Soboth, Styria, Ochozk. That these micas are not mixtures of pure potassium-mica (singulosilicate) with magnesium-mica is evident from the fact that the magnesium-micas, as well as these potassium-micas, are compounds of 1 mol. bisilicate with 3 mols. singulosilicate, and that the iron magnesium micas are singulosilicates.

Second Series.—1 mol. bisilicate to 1 mol. singulosilicate. $R'_6Si_2O_7 = R'_2SiO_3 + R'_4SiO_4$. (In part),



C. *Lithium Micas.*—Compounds of 1 mol. singulosilicate with 3 mols. bisilicate, $R'_{10}Si_4O_{13} = 3R'_2SiO_3 + R'_4SiO_4$, viz.:—

Rozena and Paris (Maine),



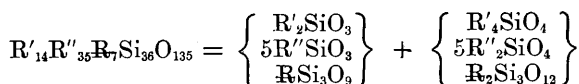
II. **MAGNESIUM MICAS.**—These micas contain the maximum amount of magnesia (nearly 30 per cent.), and are nearly or quite free from iron. They are essentially distinguished from the iron magnesium micas by their higher proportion of acid (up to 44 per cent.); they are white or light-coloured.

Compounds of 1 mol. bisilicate with 3 mols. singulosilicate, $R'_{14}Si_4O_{15} = R'_2SiO_3 + 3R'_4SiO_6$. In all of them $R : R'' = 1 : 5$, so that their formula is:—

* $R^{vi} = Al_2, Fe_2, \&c.$

† Combined.

‡ Hygroscopic.



- Newly analysed: (1.) Rossie, New York; yellow, six-sided prisms.
 (2.) Gouverneur, St. Lawrence Co., New York; light brown.
 (3.) Pargas; brownish.

	F.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	K ₂ O.
(1.)	5·11	43·17	13·43	—	1·51	27·47	8·73
(2.)	5·67	43·00	13·27	1·71	—	27·70	10·32
(3.)	4·59	42·55	12·74	1·31	0·49	27·62	8·92

	Na ₂ O.	H ₂ O.*	H ₂ O.†	
(1.)	0·92	0·40	—	= 101·04
(2.)	0·30	0·38	—	= 102·35
(3.)	1·18	1·18	0·32	= 100·90

These micas contain 1 mol. of fluosilicate to 18—20 mols. oxyasilicate. Micas belonging to this group are also found in Jefferson Co., New York; at Edwards, St. Lawrence Co., New York; at Pennsbury, in Pennsylvania; and at Ratnapura, Ceylon.

III. IRON MAGNESIUM MICAS and IRON MICAS.—Singulosilicates. Colour, dark to apparently black. The amount of magnesium may diminish till it nearly vanishes, whilst the amount of iron increases; but the two elements do not stand to one another in any definite relation. The principal differences between the individual members of this group are determined by the varying ratio of $R' : R'' : R$: hence the following subdivisions:—

First Series.— $R'_2R''_4R_8Si_4O_{16} = R'_4SiO_4 + 4R''_2SiO_4 + R_2Si_3O_{12}$
 Newly analysed: (1.) Monzoni. (2.) Arendal.

	F.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	K ₂ O.
(1.)	0·53	41·70	16·86	2·23	1·88	0·86	24·70	8·93
(2.)	1·49	38·89	14·53	4·58	7·85	1·06	20·28	10·08

	Na ₂ O.	H ₂ O.	
(1.)	0·28	1·14	= 99·11
(2.)	0·40	0·94	= 100·10

To the same group belong micas from Vesuvius (Rammelsberg found 0·65 per cent. water; Berwerth found 4 per cent.); Morawitz; Tschebarkul, Siberia; Greenwood furnace, Orange Co., N.Y.; Mainland, Shetland Isles; certain Scotch micas, according to Heddle's analyses.

Second Series.— $R'_4R''_6R_2Si_7O_{28} = R'_4SiO_4 + 3R''_2SiO_4 + R_2Si_3O_{12}$.

Newly analysed: (1.) Miask. (2.) Filipstad, Sweden. (3.) Sterzing, Tyrol. (4.) Persberg, Sweden.

* Combined.

† Hygroscopic.

	F.	TiO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.
(1.)	1·61	4·03	32·49	12·34	6·56	23·60	1·53	5·29
(2.)	1·15	—	38·20	15·45	8·63	8·69	0·90	18·08*
(3.)	trace	—	39·82	19·25	2·62	4·62	1·11	21·41†
(4.)	0·44	2·12	37·77	15·96	6·63	14·43	—	12·26

	K ₂ O.	Na ₂ O.	H ₂ O.‡	H ₂ O.§
(1.)	9·59	0·88	2·42	1·31 = 101·65
(2.)	9·17	0·18	2·94	— = 103·39
(3.)	8·33	0·66	1·69	0·18 = 99·69
(4.)	8·23	0·27	2·67	— = 100·78

Also from New York, Greenland, Servance in the Vosges, Brevig.

Third Series.— $R'_2R''_2R_2Si_5O_{12} = R'_4SiO_4 + 2R''_2SiO_4 + R_2Si_3O_{12}$.

Newly analysed: (1.) Hitterö in Norway. (2.) Renschthal in the Schwarzwald.

	F.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	K ₂ O.	Na ₂ O.
(1.)	1·29	39·01	15·44	9·37	13·67	11·30	8·62	0·14
(2.)	trace	37·79	18·79	6·48	15·28	9·72	8·93	1·92
	H ₂ O.‡		H ₂ O.§					
(1.)	2·93		0·12		= 101·89			
(2.)	2·33		—		= 101·24			

Also: Freiberg (black mica from grey gneiss); Lierwiese in the Eifel; Portland, Connecticut; Radauthal, in the Hartz. Further, micas from Scotland, according to Heddle, partly lepidomelane, partly haughtonite.

Fourth Series.— $R'_2R''_2R_2Si_5O_{20} = R'_4SiO_4 + 3R''_2SiO_4 + 2R_2Si_3O_{12}$.

A titaniferous, but nearly pure iron mica, black with green translucence. (1.) Brevig. (2.) St. Dennis.

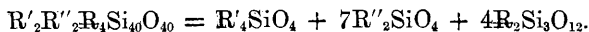
	F.	TiO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	K ₂ O.
(1.)	1·29	2·42	32·97	11·88	16·48	20·72	3·64	1·08	8·03
(2.)	4·23	—	37·93	24·89	7·85	14·87	—	0·28	8·64
	Na ₂ O.		H ₂ O.						
(1.)	0·30		3·35		= 102·16				
(2.)	0·40		1·54		= 100·63				

Of the 3·5 per cent. water in (1), only 0·5 per cent. is regarded as essential. To this series also belongs the iron mica from Wiborg.

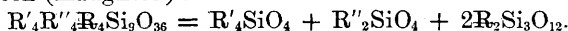
Fifth Series.— $R'_4R''_4R_4Si_9O_{36} = 3R'_4SiO_4 + 3R''_2SiO_4 + 4R_2Si_3O_{12}$. This composition was exhibited by a brown-black iron mica from St. Dennis, in Cornwall. To the same series belongs also a mica from Persberg, designated by Hausmann as lepidomelane.

Isolated amongst micas, comparatively poor in magnesia, and consisting of singulosilicates, are the following:—

Mica from Tonalite (Baltzer):



Aberdeen (Haughton):



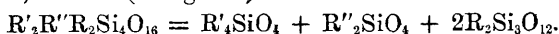
* Including 1·5 CaO.

‡ Combined.

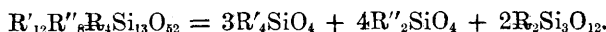
† Including 1·41 BaO.

§ Hygroscopic.

Ballyelin, Ireland (Haughton):



Brevig (Scheerer).—A black mica with $4\frac{2}{3}$ per cent. titanic acid, accompanying astrophyllite:—



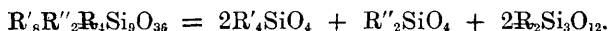
IV. LITHIUM IRON MICAS.—The mica of this group from Zinnwald is a compound of 2 mols. bisilicate with 1 mol. singulosilicate. $R_6Si_4O_{16} = 2R''_2SiO_4 + R'_4SiO_4$. The analyses of the mineral by Rammelsberg and by Berwerth both lead to this general formula. The special formulæ, based severally on the proportion (1) $R' : R'' : R : Si = 2 : 0.8 : 1 : 3.6$; or (2) $= 2 : 0.66 : 1 : 3.5$, are as follows:—

$$(1.) R'_{16}R''_4R_5Si_{18}O_{60} = 2 \left\{ \begin{array}{l} 5R'_2SiO_3 \\ 4R''SiO_3 \\ 5R_2Si_3O_9 \end{array} \right\} + \left\{ \begin{array}{l} 5R'_4SiO_4 \\ 4R''_2SiO_4 \\ 5R_2Si_3O_{12} \end{array} \right\}$$

$$(2.) R'_{12}R''_4R_6Si_{21}O_{70} = \left\{ \begin{array}{l} 3R'_2SiO_3 \\ 2R''SiO_3 \\ 3R_2Si_3O_9 \end{array} \right\} + \left\{ \begin{array}{l} 2R'_4SiO_4 \\ 2R''_2SiO_4 \\ 3R_2Si_3O_{12} \end{array} \right\}$$

16—12 mols. oxyasilicate are present to 1 mol. fluosilicate.

V. BARIUM MICA.—This white mica from Sterzing, containing 6 per cent. baryta and small quantities of iron and magnesium, is like the accompanying brown mica (p. 536), a mixture of singulosilicates.



Its analysis gave:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO (Mn).	MgO.	BaO.	CaO.	K ₂ O.
42.90	32.40	trace	2.40	3.10	5.82	0.80	7.47
		Na ₂ O.	H ₂ O.				
		1.73	3.02				

$$= 99.64$$

The analysis by Bergmann of a barium mica from the Habachthal leads on the other hand to the formula of a compound of 1 mol. singulosilicate and 1 mol. bisilicate.

H. W.

Euphotide of Elba. By A. COSSA (*Jahrb. f. Min.*, 1881, 1, Ref. 198).—The rock examined was from the great mass of euphotide on the west side of the Gulf of Pracchio. It consists of diallage and labradorite, the latter being in the larger proportion.

Analysis gave: (1.) Diallage. (2.) Labradorite:—

	SiO ₂ .	CaO.	MgO.	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Cr ₂ O ₃ .
(1.)	49.60	20.34	16.49	6.73	—	5.05	0.55
(2.)	50.63	11.00	trace	—	1.41	29.99	—
(3.)	50.68	14.05	—	—	—	31.73	—
	Mn ₂ O ₃ .	Na ₂ O.	K ₂ O.	H ₂ O.			
(1.)	trace	—	—	1.49			100.25
(2.)	—	4.77	0.23	0.99			99.02
(3.)	—	3.54					

No. 3 gives the composition of a felspar containing 70 per cent. anorthite, and an amount of silica nearly equal to that of the felspar under examination.

Both minerals appear to have been somewhat weathered, as shown by the amounts of water. The felspar stands, according to Tschermak's theory, on the limit between the labradorite and bytownite series, and answers nearly, so far as its proportion of silica is concerned, to a mixture of 65—70 per cent. anorthite, and 35—30 per cent. albite, but contains too little lime and too much alkali for such a mixture.

H. W.

Analysis of Amphibole from Amelia Co., Virginia. By F. A. MASSIE (*Chem. News*, 42, 194).—This mineral was found accompanying asbestos in the form of light green crystals, which are generally about 1 to 2 mm. long, and $\frac{1}{2}$ to 1 mm. through laterally. The angle $I \wedge I = 124^\circ 30'$ was repeatedly obtained with the microgoniometer, as also the same angle between cleavage planes. Hardness = nearly 6; sp. gr. 3.041; lustre vitreous; streak almost white; as transparent as green window glass; fusible with difficulty before the blowpipe flame. Analysis gave:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.
56.96	4.32	2.45	2.24	22.33	11.44	0.31

corresponding with the formula $(\frac{11}{14} R'' + \frac{2}{14} R''') \text{SiO}_3$, that of a meta-silicate, mainly of magnesium and calcium, with a certain amount of isomorphous replacement of dyad and triad iron by aluminium.

D. B.

Lime Iron Garnet ("Demantoid"), from Sysertzk in the Urals. By A. LÖSCH (*Jahrb. f. Min.*, 1879, 785—791).—The author describes the locality and the mode of occurrence of this mineral, and some results obtained in its examination. Its true nature has only been known some four years, it having been very generally considered as chrysolite by lapidaries. It occurs in clefts in a peculiar serpentine-like rock with dolomite, clay, magnetic iron, and serpentine asbestos. The grey or greyish-green rock contains small earthy particles and black grains, the ground-mass being an irregular aggregate of radiating plates of a colourless rhombic mineral, having a composition similar to serpentine; there are also dolomite, green garnets, chrome and magnetic iron in small grains dispersed throughout. The imbedded garnets are generally elongated in form, or lie close together as though pressed against each other, but separated by films of serpentine, still much more generally in irregular modules, $\frac{1}{4}$ —2 inches in diameter. These latter consist of a great number of quite irregularly grouped particles lying close to one another, but always separated by serpentine films. So far only one definite garnet crystal has been found, it shows the forms ∞O . 202, but its faces and edges are imperfect and rounded. The crystals of magnetic iron, ∞O , are likewise, but very imperfectly developed, and this the author considers to be produced by the resistance of the medium in which the crystals have

been formed. The garnets examined microscopically are perfectly pure and structureless; in colour they are emerald-green to a rather deep yellowish-brown, generally of a light yellowish-green. When polished they show a splendid play of colours, owing to their perfect transparency and high index of refraction; and were it not for insufficient hardness (somewhat less than that of quartz) and occurrence in small pieces, it would become a much valued precious stone. It fuses with great difficulty, and is decomposed easily by acids with separation of flaky silica. The means of two analyses of (1) a light grass-green variety, and of (2) a deep emerald-green variety are:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.
(1.)	35.56	0.57	30.80	0.64	33.05	0.16 = 100.78
(2.)	35.50	0.70	31.51		32.90	0.21 = 100.82

No. 2 contained a small quantity of chromium, which was not the case with No. 1. Sp. gr. = 3.838. A quantity on fusion in a furnace lost 0.33 per cent., and contained 2.82 per cent. more iron as FeO than the original mineral; the fused mass was brittle, and but slightly transparent.

H. B.

Hypersthene from Bodenmais. By F. BECKE (*Jahrb. f. Min.*, 1881, 1, Ref. 195).—This mineral (described by Kenngott as ficinite) occurs in fragments and crystals up to 4 cm. long, intergrown with the well-known minerals occurring at Bodenmais, especially with magnetic pyrites. Colour black-brown. Streak light brownish. Lustre vitreous to pitchy on the natural faces. Hardness = 6. The crystals are rhombic. Observed faces $\infty P\infty$, $\infty P\infty$, $0P$, ∞P , ∞P^2 , $\frac{1}{2}P\infty$, $\frac{1}{4}P\infty$, $\frac{1}{8}P\infty$, $\frac{1}{2}P^2$, $\frac{1}{2}P$, $\frac{3}{4}P^{\frac{3}{2}}$. The optical properties agree with those of other hypersthene.

Microscopic examination shows but few inclosed minerals, a small quantity of magnetic pyrites being however visible to the naked eye. Sp. gr. 3.449; after deduction of 1.2 per cent. magnetic pyrites, 3.439.

In the following table I, is the direct result of analysis; II, the composition calculated to 100°, after deduction of admixtures (magnetic pyrites and apatite); III, the composition calculated from the formula given below:—

SiO ₂ .	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.
48.86	0.42	1.92	4.80	12.43	5.32	21.07
51.23	—	2.02	5.04	13.02	5.58	22.08
50.83	—	1.96	4.59	13.70	5.40	22.46
Magnetic pyrites.						
CaO.	H ₂ O.					
1.48	1.35	1.20 = 98.85				
1.03	—	— = 100				
1.06	—	— = 100				

The formula is 2(SiO₂, Al₂O₃, MgO) + 3(SiO₂, Fe₂O₃, MgO) +

$2(\text{SiO}_2, \text{CaO}, \text{MgO}) + 26(2\text{SiO}_2, 2\text{MgO}) + 10(2\text{SiO}_2, 2\text{FeO}) + 4(2\text{SiO}_2, 2\text{MnO})$. Remarkable is the large amount of Fe_2O_3 required by the term $\text{SiO}_2, \text{Fe}_2\text{O}_3, \text{MgO}$. In consequence of incipient weathering, the analysis gives somewhat too much Fe_2O_3 , and somewhat too little FeO . H. W.

The Dunite of the Jenks Mine, Macon Co., N. Carolina. By R. W. RAYMOND (*Jahrb. f. Min.*, 1880, 2, Ref. 302).—This rock occurs, rarely stratified, in Laurentian crystalline slates. It is crystalline, and in some places exhibits an apparent stratification, which, however, does not accord with that of the neighbouring rock; it contains separated crystals of magnetite and chromite.—*Analyses*. 1. From Webster by Genth.—2. From Culsagee by Chatard :—

SiO_2 .	Al_2O_3 .	FeO .	NiO .	MgO .	CaO .	Loss by ignition.	Chro- mite, &c.	
41.89	trace	7.39	0.35	49.13	0.06	0.82	0.58	= 100.22
41.58	0.14	7.49	0.34	49.28	0.11	1.72	—	= 100.66

The dunite of the Jenks mine contains five parallel layers of chlorite, varying in thickness from a few inches to several feet, which contain the greater part of the corundum. In each of these zones, the corundum appears in a different variety, these varieties being distinguished chiefly according to colour and transparency, viz., ruby, sapphire, asteria, emery, amethyst, girasol, chatoyant, and white sapphire. The exploration of corundum in the Webster and Culsagee mines is for the present discontinued. H. W.

Minerals of the Clay Group. By R. HELMHACKER (*Jahrb. f. Min.*, 1880, 2, Ref. 296).—(1). *Halloysite* from the Kozla mine, near Drenkova in the Bannat, where it forms a layer in a coal-seam of the lower lias. Imperfectly scaly, with a strong vitreous lustre; light wax-yellow scales, translucent at the edges, alternating with yellowish-white opaque scales having a fainter lustre, the two varieties, however, being united by others of intermediate character. Fracture imperfectly conchoidal, coarsely splintery. Adheres slightly to the tongue. The compact mineral, when immersed in water, gives off bubbles of air. When heated, it gives off water and turns white, afterwards becoming dark grey and giving off an empyreumatic odour, indicating the presence of organic matter. Before the blowpipe, it burns white again, without melting. Dissolves in acids with separation of flocculent silica. Hardness = 2.5; after ignition 4. Sp. gr. 1.962 to 1.985 (determined after leaving the mineral for several weeks in the exsiccator over sulphuric acid). The mineral gives off 10 per cent. water over sulphuric acid; 18 per cent. at 220° ; 28.9 per cent. at a red heat. Two specimens dried over sulphuric acid gave, by analysis :—

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	H_2O^* .	$\text{H}_2\text{O}^\dagger$.	
(1.)	40.19	34.84		2.55	8.08	15.27	= 100.93
(2.)	36.34	32.07	0.27	2.31	10.59	18.29	= 99.87

* At 100° .

† Above 100° . The mineral contains also traces of MgO , MnO , and P_2O_5 .

After deduction of admixed calcite, analysis (1) gives the formula $\text{Al}_2\text{Si}_2\text{O}_7 + 3\text{aq}$, and analysis (2) gives $\text{Al}_2\text{Si}_2\text{O}_7 + 4\frac{1}{2}\text{aq}$, for the air-dried substance; for the substance dried at 100° , the quantities of water are 2aq and $2\frac{1}{2}\text{aq}$, respectively. Although this mineral, when dried at 100° , has the same composition as kaolin, the two must nevertheless be regarded as distinct, inasmuch as halloysite is amorphous, whereas kaolin is made up of microscopic crystals.

(2). *Schrötterite* from Freienstein, near Leoben. The fragments of the mineral so-called, occurring here and there on an old heap of mining refuse, were found to consist of transparent colourless halloysite having a vitreous lustre, and opaque, chalk-white variscite having a dull aspect and earthy fracture. The halloysite differs from that from the Bannat above described, both by its colour and by the fact that after drying over sulphuric acid, it falls to pieces with a slight noise when thrown into water, a property connected with the existence of numerous microscopic fissures. Analysis gave numbers leading to the formula $\text{Al}_2\text{Si}_2\text{O}_7 + 4\frac{1}{2}\text{aq}$; when dried at 100° the mineral contains $2\frac{1}{2}\text{aq}$. Sp. gr. = 2.143 . It gives off 3.93 per cent. water over sulphuric acid, 10.9 at 100° , and 28.5 at a red heat.

The *variscite* has a hardness = 2, dissolves readily in acids, glows somewhat brightly before the blowpipe, and is infusible; when immersed in water, it becomes translucent with pale greenish colour. Sp. gr. = 2.140 . Analysis gave:—

P_2O_5 .	Al_2O_3 .	Fe_2O_3 .	CuO .	CaO .	MgO .	SO_3 .
25.69	34.46	0.34	0.11	1.56	0.10	0.49
	SiO_2 .	H_2O^*	$\text{H}_2\text{O}^\dagger$			
	2.80	16.11	17.57 = 99.23			

After deduction of gypsum, calcite, and brown iron ore, and of quantities of Al_2O_3 and H_2O equivalent to 2.80 per cent. silica, due to admixed halloysite, these numbers led to the formula $5(\text{Al}_2\text{P}_2\text{O}_8 + 4\text{H}_2\text{O}) + 4\text{Al}_2\text{H}_2\text{O}_4$, i.e., to that of a mixture of 5 mols. variscite and 4 mol. diaspore. As a chemical combination of this kind is by no means probable, the mineral may be regarded as a mechanical mixture of variscite and diaspore.

(3). *Montmorillonite* from Macskamező, near Podurnoj in Transylvania. Pale rose-red, translucent at the edges; falls to pieces in water. H. = 1. Sp. gr. = 2.52 . Melts before the blowpipe to a white enamel. Insoluble in acids. Amount of water variable. Analysis of the mineral (certainly not pure) gave $\text{Al}_4\text{Si}_7\text{O}_{20}$ with $2\frac{3}{4} - 3\text{aq}$.

(4). *Razumowskyn* and *Pyrophyllite*.—The blue or green mineral from the Lavant valley in Carinthia, named allophane by Riedl, was found to be a variable aggregate of several argillaceous minerals with foreign admixtures. Two of these aggregates were analysed, and one of them was found to consist mainly of razumowskyn, the other of pyrophyllite.

The razumowskyn is either transparent with vitreous lustre, and bluish from admixed azurite, or only translucent and greenish from

* Given off at 100° .

† Above 100°

admixed malachite; in a thin section, colourless constituents are recognisable, together with the coloured admixtures. Cold hydrochloric acid dissolves out the coloured copper carbonates, leaving a white translucent clay, which is not attacked till afterwards. Before the blowpipe, the mineral blackens, but becomes greyish-white after prolonged heating. Hardness nearly 3. Sp. gr. of several specimens 2.285 to 2.229. The mineral placed over sulphuric acid gives up 6.5 to 10 per cent. water, and the dried substance falls to pieces when immersed in water. It gives off 8.4 per cent. water at 100°, and 15.4 at 160°. The dried mineral, when exposed to the air, reabsorbs water, which, with the exception of the last portions, is given off more quickly and at a lower temperature than at the first drying. The same peculiarity is exhibited by the halloysite from Kozla. Two analyses gave:—

	SiO ₂ .	Al ₂ O ₃ .	CuO.	CaO.	MgO.*	H ₂ O.*	H ₂ O.†
I..	43.06	25.26	3.25	0.83	trace	8.44	20.10 = 100.94
II..	41.94	25.55	5.77	1.80	trace	9.35	15.16 = 99.57

According to I, the air-dried mineral is a mixture of 94 per cent. razumowskyn ($\text{Al}_2\text{Si}_2\text{O}_7 + 6\text{aq}$), with $1\frac{1}{2}$ per cent. calcite and $4\frac{2}{3}$ azurite; according to II, it is a mixture of $89\frac{2}{3}$ per cent. razumowskyn, with 2 per cent. calcite and $8\frac{1}{3}$ azurite.

The *pyrophyllite* is opaque, white, with a bluish or greenish tinge, nearly lustreless; adheres to the tongue; infusible. Hardness $1\frac{1}{2}$ to 2. Sp. gr. 2.576. It gave off 7 to 8 per cent. water in the exsiccator, 1.2 per cent. at 100°, 2.2 at 250°, 15.5° at a red heat. Analysis gave:—

SiO ₂ .	Al ₂ O ₃ .	CuO.	CaO.	H ₂ O.*	H ₂ O.†
43.98	37.84	1.66	trace	0.86	15.71 = 100.05

leading to the formula $4(\text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}) + \frac{1}{2}\text{aq}$, which is that of kaolin with a slight excess of water. As, however, this clay is partly decomposed by hydrochloric acid, and its particles when examined by the microscope do not exhibit any hexagonal outlines, it cannot be regarded as kaolin. From a partial analysis of the extract obtained with dilute hydrochloric acid, and of the residue, it appears probable that the clay is a mixture of predominating pyrophyllite with allophane, and perhaps a small quantity of razumowskyn. H. W.

Report on the Minerals of some of the Apatite-bearing Veins of Ottawa Co., Quebec, with Notes on Miscellaneous Rocks and Minerals. By B. J. HARRINGTON (*Geol. Survey of Canada*, 1879; *Jahrb. f. Min.*, 1881, 1, Ref. 32).—These veins occur in almost exclusively augitic rocks, containing small quantities of quartz and orthoclase, sometimes also mica and small garnets, having mostly the appearance of massive eruptive rocks, and occurring together with gneisses, quartzes, and granular limestones. The apatite often occurs in the augitic rock in true lodes, which sometimes have an elongated structure, but are mostly quite irregular. The apatite-crystals, often

* Given off at 100°.

† Above 100°.

broken and cemented together again, are in some places a foot and more in diameter, several feet long, and weigh several hundred-weight; their edges and summits are often rounded. In other places the mass is compact to coarsely granular; a friable saccharo-granular variety is common. A sea-green mass was found almost free from other minerals, and having a diameter of nearly 20 feet. The colour is very various, green of various shades, sky-blue, red, brown, yellow, and white. Sp. gr. of a dark green variety, 3·2115.

Thirty minerals have been found in the apatite beds, especially quartz, calcspar, augite, hornblende, magnesia, mica, garnet, black tourmalin, titanite, zircon, orthoclase, scapolite. The most common of these accompanying minerals is an augite, viz., an aluminiferous sahlite; a light-coloured variety is also common. The augite is often converted externally, either wholly or partially, into uralite.

The following table contains the analyses—A, of the centre of a vitreous augite crystal; B, of its dull dark crust; C, of an aggregate of hornblende (uralite) prisms; D, of a blackish-green crystal of augite:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.
A. . . .	50·87	4·57	0·97	1·96	0·15	24·44	15·37	0·50
B. . . .	50·90	4·82	1·74	1·36	0·15	24·39	15·27	0·15
C. . . .	52·82	3·21	2·07	2·71	0·28	15·39	19·04	0·69
D . . .	51·28	2·82	1·32	9·16	0·33	23·34	11·61	—

	Na ₂ O.	Loss by ignition.	Sp. gr.
A	0·22	1·44 = 100·49	3·181
B	0·08	1·20 = 100·06	3·205
C.	0·90	2·40 = 99·51	3·003
D	—	0·17 = 100·03	3·385

The most remarkable point in the transition from A to C is the decrease of lime and increase of magnesia.

These Canadian apatite beds exhibit considerable analogy to the Norwegian beds described by Brögger and Reusch. H. W.

Mineralogical Observations. By H. LASPEYRES (*Zeitsch. f. Kryst.*, 4, 244—256; *Jahrb. f. Min.*, 1881, 1, Ref. 17).—The sericite of Hallgarten in the Rheingau, is not a distinct mineral, but a dense potash mica. The essential part of it indeed was found to dissolve completely although slowly in boiling hydrochloric acid, whereby a certain quantity (about 11 per cent.) of microscopically recognisable quartz mixed with it was separated. The analysis of the soluble portion, calculated on the pure substance dried at 105° gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.
45·361	32·919	2·048	1·762	0·494	0·895	11·671
		Na ₂ O.	H ₂ O.			
		0·724	4·126 = 100.			

The mineral has therefore the composition of a potash mica, R'₂(Al₂)^{vi}Si₂O₈.

That sericite has not the hardness and elasticity of mica is due to its peculiar texture and structure: it is evident, indeed, that a group of microscopic scales cannot retain the properties of macrocrystalline individuals. The specific gravity, on the other hand, remains unaltered, that found for sericite, viz., 2·8091, being also that of potash mica. The very slight chromatic polarisation of sericite, which has been regarded as a character distinguishing it from mica, is due to the extreme thinness of the plates; very finely pulverised mica, in fact, does not polarise more strongly than sericite. This mineral is, therefore, related to potash mica in the same manner as talc to steatite or alabaster to gypsum. Laspeyres supposes that it has been produced by transformation of feldspars. H. W.

Notices on some Austrian Minerals. By SCHARIZER (*Jahrb. f. Min.*, 1881, 1, 23).—1. *Crystalline Form of Columbite*.—The crystal examined was from the granite of the Austrian side of the Riesengebirge; it was 4 cm. long, 2 cm. broad, and exhibited the forms $P, \infty P\infty, \infty P\infty, 0P, 2P_2, \infty P_3, \infty P_6$.

2. *Pyrope and serpentine*, found at Krempe, in the Bohemian Forest. The pyrope formed blood-red rounded grains, varying in size from that of a millet-grain to that of a pea, lying in a light- or dark-green serpentine, and surrounded by a grey envelope (kelyphite, according to Schrauf). The true composition of pyrope is given by the analysis of the red grains—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Cr ₂ O ₃ .	FeO.	CaO.	MgO.
40·45	19·67	4·05	2·60	6·90	5·78	20·79 = 100·24

This analysis leads to the garnet-formula $R'_3R''_2Si_3O_{12}$, specially $(Mg_{26}Ca_5Fe'_2)(Al_{20}Fe''_2Cr_2)Si_{36}O_{144}$.

The *serpentine* (sp. gr. 2·906), which forms the matrix of the pyrope, exhibits a varying amount of H₂O and Fe, the proportions of which decrease as that of magnesium diminishes, and *vice versâ*. Analysis of lumps free from magnetite gave—

SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.
40·46	0·50	1·53	8·85	2·49	35·67	10·52 = 100·02

leading to the formula $7SiO_2, 11RO, 6H_2O = 3(3RO, 2SiO_2, 2H_2O) + 2(RO, SiO_2)$, so that this serpentine appears to be a mixture of 3 mols. pure serpentine with 1 mol. undecomposed olivine; and this view of its composition is confirmed by the examination of thin sections.

3. *Pseudomorph after Garnet*.—The specimen examined was a fragment of a crystal as large as the fist, from the Otzthal, consisting of a nucleus of pure almandin, 1·3 per cent. MgO, 3 CaO, 18·5 Al₂O₃, and 41·05 SiO₂, coated with a layer of a dark-green chloritic mineral 5 mm. thick, greasy to the touch, and having the composition—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CO ₂ .	Mn.	H ₂ O.
24·24	22·13	18·73	12·34	9·02	traces		12·67 = 99·13

which agrees tolerably well with that of the aphrosiderite of Mittershausen in Nassau, analysed by Erlenmeyer. H. W.

Canadian Minerals. By C. HOFFMANN (*Chemical Contributions to the Geology of Canada*, Montreal, 1880).—*Cyanite* from the North Thompson River, British Columbia. Imbedded, together with silvery-white mica, in granular quartz. Forms radiated columnar aggregates. Colour in parts blue, passing into greenish-grey, rarely almost colourless; the rest of a uniform light bluish-grey. Lustre vitreous, subtransparent. Sp. gr. = 3·6005. Dried at 100° it contained—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.
36·288	62·254	0·552	1·064	0·355 = 100·513

Lazulite.—Found three-quarters of a mile east of the mouth of the Churchill River, district of Keewatin. Massive, in veins traversing quartz. Colour deep azure-blue. Lustre vitreous. Fracture uneven. Brittle. Streak white. Subtranslucent. Hardness nearly 5·5. Sp. gr. 3·0445. Colours the blowpipe flame pale bluish-green; swells up, whitens, and falls to pieces, but does not fuse. The composition of the mineral dried at 100° (exclusive of 3 per cent. of silica) is as follows:—

P ₂ O ₅ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.
46·388	29·440	2·091	13·838	2·829	6·468 = 100·754

Graphite.—A specimen of disseminated graphite from the “Split Rock Plumbago Mine,” near St. John’s River, New Brunswick, was found to contain 44·775 per cent. graphitic carbon, 50·058 rock-matter, and 1·167 hygroscopic water. The compressed graphite gives a fairly black and shining streak, and is adapted for the manufacture of the commoner kinds of lead-pencils.

Infusorial Earth, or *Earthy Tripolite*.—This substance occurs in considerable quantity in the Pollet River Lake, King’s County, New Brunswick, forming a deposit 4 feet deep, and apparently of fresh water origin. In texture, it resembles an earthy chalk; very fine-grained, but harsh to the touch; adheres to the tongue. It has a light greyish-white colour, but when heated in a closed tube becomes dark grey from separation of carbon, and gives off an abundance of a somewhat ammoniacal light brownish-yellow water, showing that it contains nitrogenous organic matter. When ignited with free access of air, it turns white. On digesting it, either before or after ignition, with boiling potash-solution, the silica readily dissolves, leaving a small amount of residue of a light reddish-brown colour after ignition.

An analysis of the air-dried substance gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	CO ₂ .	X.*
81·49	3·15	0·95	0·34	0·28	0·01	13·32 = 99·54

This infusorial earth forms an excellent polishing material, and will probably be found well adapted for the preparation of dynamite and of water-glass.

Kaolin.—This material occurs at Grand Frenier, County of Two

* Water, combined and hygroscopic, and organic matter. The amounts of potash and soda were not determined.

Mountains, Quebec, in a dyke from 1 to 2 feet thick, dipping northward at an angle of about 50° , and cutting through flat massive beds of sandstone. The sample examined was in compact friable masses, greasy to the touch, of fine earthy texture, and adhering to the tongue. Colour light brownish-yellow, mottled with white. Forms an exceedingly plastic paste with water. Dried at 100° it gives—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Cr ₂ O ₃ .	TiO ₂ .	CaO.	MgO.
32.01	29.91	14.02	0.55	9.56	0.41	0.25
<u>K₂O. Na₂O.</u>			H ₂ O.			
traces			13.005	= 99.715.		

On carefully washing the clay, a very small quantity of a heavy black granular powder was left, consisting mainly of chromite. It contained also a small quantity of titanite acid. The clay bears an incipient white heat without the least signs of fusion; at the same time it becomes hard, tough, and sonorous, purplish-brown externally, blackish-brown in the mass.

Alunogen.—This mineral was found on an old heap of shale at the Scotia Mine, Springhill Coal-field, Cumberland Co., Nova Scotia, forming a crust of $5-5\frac{1}{2}$ cm. thick. Colour white, in some parts light yellow. Taste, inky—astrigent. Melts in its water of crystallisation, and gives off sulphuric acid at a higher temperature. Soluble in water. An analysis by F. D. Adams gave—

SO ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.
36.935	13.479	2.888	0.157	0.140	0.138	0.087	0.131
H ₂ O.			Insol.				
45.109			0.235	= 99.299.			

There was also a small quantity of ammonia, the amount of which was not determined.

Iron Ores.—Four specimens of magnetite from various localities gave from 45.86 to 48.06 per cent. metallic iron. A specimen of bog iron ore from Thurlow, Hastings County, Ontario, gave 48.53 per cent.

Copper Ores.—Copper-glance, from Spar Island, Lake Superior, yielded 38.24 per cent. copper. Copper pyrites from the north side of Echo Lake, District of Algoma, yielded 18.74 per cent. A bluish-black magnetite containing a little copper-pyrites from Queen Charlotte Island, British Columbia, yielded 1.89 per cent. copper.

Manganese Ores.—An ore from Boalarderie Island, Cape Breton, Nova Scotia, gave, after drying at 100° , 11.04 per cent. MnO₂, 12.49 Fe₂O₃, and 57.76 insoluble matter, together with small quantities of copper, nickel, and cobalt.

Gold and Silver Assays.—The following table shows the amounts of gold and silver (in ounces per ton of 2,000 lbs.) found in various Canadian minerals:—

black. Does not colour boiling potash. Coke, pulverulent. Ash, almost white. 5. Locality about 18 miles up the Watsonquah River, British Columbia.—Very compact, homogeneous, hard, brittle. Does not soil the fingers. Colour, black, with slight brownish tinge. Lustre, dull resinous. Fracture, conchoidal. Takes fire in a lamp-flame, but does not burn long after removal. Heated in a covered crucible, it produces a very large amount of flame. In the closed tube, it yields a considerable quantity of tarry matter. Powder does not colour boiling potash. Gives a firm coke when quickly heated. Ash, light reddish-brown: altogether an excellent coal.

The following table exhibits the results of analysis of these coals, obtained by slow and by fast coking:—

	Hygroscopic water.	Volatile combustible matter.	Fixed carbon.	Ash.	Ratio of volatile combustible matter to fixed carbon.
1. s. ...	3·73	28·01	54·28	13·98	1 : 1·94
f. ...	3·73	34·33	47·96	13·98	1 : 1·40
2. s. ...	6·26	29·31	55·70	8·73	
f. ...	6·26	31·96	53·05	8·73	
3. s. ...	1·05	15·35	42·70	40·90	1 : 2·78
f. ...	1·05	19·09	38·96	40·90	1 : 2·04
4. s. ...	1·52	7·63	45·61	45·24	1 : 5·97
f. ...	1·52	7·20	46·04	45·24	1 : 6·39
5. f. ...	—	40·52	57·51	1·97	

H. W.

Contributions to Mineralogy. By G. VOM RATH (*Zeitsch. f. Kryst.*, 5, 1; *Jahrb. f. Min.*, 1881, 1, Ref. 181—195).—1. *The crystal-system of Cyanite.*—2. *Galena from the Morgenstern mine, Kreis Laasphe, in Westphalia.*—3. *Ores, especially Bismuth-ores, from the District of Tazna in Bolivia.*—According to Domeyko, Bolivia is the richest in bismuth of all countries in the world. The following ores are especially noticed:—*a.* Bismuth-glance. On prismatic crystals Groth found the hitherto unobserved terminal faces, $P\infty$, with an angle of nearly 90° , so that $b:c$ is nearly as 1:1. *b.* Jamesonite. $S = 21\cdot72$; $Pb = 39\cdot04$; $Fe = 6\cdot58$; $Sb = 32\cdot98$. Total, 100·32. *c.* Native Bismuth; partly changed into bismuth-ochre; when this change has not taken place, the mineral shows the well-known feathery grouping of native bismuth.

4. *Minerals from the Andesite of the Arany Berg near Deva in Transylvania.*—The following minerals are found in numerous small druses and clefts, or envelopes of other minerals:—Indymite, augite, hornblende, garnet, reddish-brown mica, magnetite, pseudobrookite, szaborite, titanite, plagioclase in twins according to the albite law, and characteristic forms; also anorthite produced by sublimation. Cry-

tallographic descriptions are given of pseudobrookite, anorthite, and plagioclase.

5. *Minerals from the Mining District of Rodna in Transylvania.*—*a.* Galena in combinations of the predominant cube with octohedrons and dodecahedrons subordinate. *b.* Zinc-blende in the forms $+\frac{O}{2}, -\frac{O}{2}, \infty O\infty, \infty O, +\frac{303}{2}$; also cerussite in its ordinary forms and twins; more rarely feather-ore, arsenical pyrites, copper pyrites, malachite, zinc-spar.

6. *Garnierite from New Caledonia.*—This mineral, produced by the decomposition of serpentine, was found to contain—

SiO ₂ .	$\frac{Fe_2O_3, Al_2O_3}{1.57}$	NiO.	MgO.	H ₂ O.
39.78	1.57	33.91	10.66	15.83 = 99.75

leading to the formula $MgNi_2Si_3O_9 + 4H_2O$, which requires 40.77 SiO₂, 33.86 NiO, 9.06 MgO, and 16.31 water.

7. *Scapolite from Monte Monzoni.*—Cauliform prisms and fibrous groups, occurring together with brownish-yellow garnet, at Le Selle on this mountain, gave:

SiO ₂ .	Al ₂ O ₃ *	CaO.	K ₂ O.	Na ₂ O.
52.19	23.54	9.61	2.11	12.65 = 100.10

Hence the mineral is nearly related to the more highly silicated varieties of scapolite, the type of which is the mizzonite of Vesuvius.

8. *Thenardite from Lake Balschasch, in Central Asia.*—On the extremely flat shores of this lake thenardite occurs in very considerable quantities. A coarsely granular crystalline mass contained in its cavities rhombic crystals, $P \cdot \infty P$, which analysis showed to consist of pure sodium sulphate.

9. *Mica from Striegau in Silesia.*—The mineral occurs on quartz in small light yellowish scales, the composition of which is given in analysis I. Analysis II gives the result of the decomposition of a mica from Hirschberg, forming a pseudomorph after felspar—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.
I..	49.27	28.69	2.89	0.42	—	13.91	—	4.77 = 99.95
II..	49.04	29.01	5.56	0.75	0.17	11.19	0.50	4.65 = 100.87

10. *Minerals from the Silberberg at Bodenmais in Bavaria.*—*a.* Orthoclase of yellowish or light leek-green colour. Observed forms, $0P, \infty P\infty, \infty P, \infty P\bar{3}, +P\infty, +2P\infty, P, 2P\infty$. *b.* Oligoclase crystals rarely larger than 3 cm., and always of a darker green than the orthoclase; often covered with a dark crust. Observed forms: $0P, \infty P\infty, \infty'P, \infty'P', \infty'P'\infty, \infty'P\bar{3}, P\infty, 2P\infty, \frac{4}{3}P\infty, P, P'\infty$. Twin-formations are also described. *c.* Cordierite in crystals of the ordinary form. *d.* Gahnite $O \cdot \infty O$. *e.* Vivianite occurs amongst the secondary minerals. *f.* Tinstone. Very rare in Bodenmais. A fine crystal intergrown with magnetic pyrites exhibited the faces $P, P\infty, \infty P, \infty P\infty, 6P6$. *g.* Hypersthene: from the Barbara mines.

* With a small quantity of Fe₂O₃.

11. *Minerals from Hühnerkobel between Zwiesel and Bodenmais.*—The pegmatite of this locality is distinguished by the occurrence of very fine minerals. The most abundant is rose-quartz, the colouring matter of which consists of titanite oxide to the amount of 1 to $1\frac{1}{2}$ per cent. Quartz is also found of greyish-white colour, associated with orthoclase, plagioclase, and mica. The quartz and the feldspars are often combined in the form of graphic granite. The following are of rarer occurrence: *a.* Triphylin, massive and in crystals, the latter not unfrequently decomposed (pseudotriplite). A crystal is described exhibiting the faces ∞P , $\infty P\bar{2}$, $\infty P\bar{\infty}$, $P\bar{\infty}$, $2P\bar{\infty}$. By alteration of the triphylin are formed: first, blue *heterosite*, then blackish-green *melanchlore*, and finally the pseudomorph called *pseudotriplite*, a mixture of green iron ore or kraurite, with ferric and manganic hydroxides and wad. *b.* Niobite, the rarest of the minerals from Hühnerkobel. The author describes a fine twin-crystal according to $2P\bar{\infty}$, the predominant face of which, $\infty P\bar{\infty}$, is vertically striated. The other faces are $\infty P\bar{\infty}$, $0P$, P , $2P\bar{\infty}$, ∞P , $\infty P\bar{3}$, $2P\bar{2}$. In the same cleft occur arsenical iron, uranium mica, and vivianite.

12. *Tourmalin from the Hörlberg.*—The crystals exhibit the ordinary forms: at the antilogous pole, R and $-2R$; at the analogous pole $-R$, $0R$; ∞R is found—a somewhat rare occurrence—with all its faces developed.

13. *Orthoclase from Frath.*—The crystals are found in pegmatite, mostly intergrown with tourmalin. They form twins according to the Carlsbad law.

14. *Minerals from Zöptau and Schönberg in Moravia.*—The formation in which these minerals are found belongs to the group of crystalline slates, viz., gneiss, mica-, talc-, and chlorite-, hornblende-, and clay-slates. The minerals described are quartz, albite, epidote, prehnite, and apatite; also zircon from the Zjdar Berg (locality of enstatite): *a.* Quartz from the Spitzberg at Wermsdorf, near Zöptau in Moravia. Observed faces: rhombohedrons of the first and second orders, $+R$ and $-R$, &c.; pyramids of the second order, $2P2$ and $P2$, the prism ∞R , and trapezohedrons. *b.* Albite. The ordinary forms and twins according to the albite law. *c.* Epidote. Very fine crystals, often in clefts of hornblende-slate; many of them have a rhombic aspect from the occurrence of $+P$ and $P\bar{\infty}$ at the ends of the axis b in equilibrium. Further, $\infty P\bar{\infty}$, $\frac{1}{2}P\bar{\infty}$, $0P$, $P\bar{\infty}$, and $-P\bar{\infty}$, these faces being enumerated in the order of their size. In other crystals $0P$ and $\infty P\bar{\infty}$ occur predominant, together with the orthodomies, and at the ends the faces $+P$ chiefly occur. The epidote is sometimes accompanied by sphene. *d.* Prehnite occurs sometimes in globular masses, sometimes in beautiful smooth-faced crystals, exhibiting the forms ∞P , $\infty P\bar{\infty}$, $3P\bar{\infty}$, and $\infty P\bar{\infty}$. The pseudomorphs of prehnite after calcspar, described by Blum, are also mentioned. *e.* Apatites. The talc- and chlorite-slates contain also yellow apatites, with prism and basal face, also well-defined green crystals of this mineral with numerous faces exhibiting the principal forms of the Alpine apatites. *f.* Zircon from the Zjdar Berg, and staurolite, andalusite and beryl from the Goldstein, near Alstadt, are also mentioned.

15. *Heavy Spar from the Basalt of the Finkenbergr, near Küdinghofen, opposite Bonn.*—A small crystal from this locality exhibited the faces $0P$, $\frac{1}{2}P\infty$, $P\infty$, $\frac{1}{2}P\infty$, ∞P , \bar{P} , $\infty P\infty$. $0P$ and ∞P are cleavage-forms. The character of the crystals is tabular, parallel to the base. As accompanying minerals, in the drusy cavities of the basalt, occur sphærosiderite and calcspar.

16. *Minerals from Chili.*—*a.* Atacamite. The crystals occur in thin tablets, filling clefts, and as coatings on brown hæmatite. They are tabular according to $\infty P\infty$, and exhibit the faces P , $P\infty$, $P\infty$, ∞P , $\infty P\bar{2}$. Angle $\infty P : \infty P = 112^\circ 55'$; $P\infty : P\infty = 106^\circ 2'$, whence $a : b : c = 0.6629 : 1 : 0.7531$, agreeing nearly with the axial ratio given by Brögger for atacamite from Chili. *b.* Tourmalin. The crystals exhibit the ordinary forms, but are especially interesting on account of their occurrence with red copper oxide and chrysocolla.

17. *Tetradymite, from Horhausen near Newwied.*—Observed faces: $\infty O\infty$, ∞O , $\infty O_3 \pm \frac{O}{2}$, $\pm \frac{2O_2}{2}$, $\pm \frac{4O_4}{2}$, $\pm \frac{\frac{3}{2}O}{2}$, $-\frac{6O_2}{2}$, $-\frac{5O\frac{3}{2}}{2}$.

18. *Tridymite from New Zealand.*—The tridymites found by Ulrich occur sometimes in very large quantities in the cavities of an andesite-lava stream, about 80 feet thick, at Lyttelton Harbour near Christchurch, in the province of Canterbury. They exhibit all the characters hitherto observed in this mineral, and are accompanied by another mineral, the nature of which has not yet been determined.

19. *Diaspore from the Greiner.*—This mineral occurs in small druses in a crystallo-laminar mass of cyanite and margarite, forming small colourless to light greenish prismatic crystals, exhibiting the faces P , $\infty P\bar{2}$, $\infty P\frac{3}{2}$, $\infty P\infty$.

20. *Minerals from the Veins of Copper-ore near Copiapo, in Chili.*—*a.* Trippkeite. A cupric arsenite, $nCuO, As_2O_3$, occurring in small bluish-green crystals, in druses of a thick bed of red copper-ore mixed with malachite and copper pyrites. The crystals are quadratic: $a : c = 1 : 0.916$. Observed forms: P , $\infty P\infty$, $0P$, $\frac{1}{2}P$, $3P$, $\frac{3}{4}P_3$, P_4 , ∞P . the first three predominant, the rest subordinate. The pyramidal faces are smooth; the basal faces only faintly lustrous. The mineral dissolves in hydrochloric and in nitric acid, and yields a button of copper on charcoal before the blowpipe. The value of n in the formula has not yet been determined. *b.* Olivenite accompanies trippkeite in radial slender needles, having an olive- to pistacio-green colour, something like epidote, and exhibiting the combination ∞P (angle $92^\circ 30'$ in front), $P\infty$ (angle $110^\circ 50'$ above), $\frac{1}{3}P\infty$, $0P$. *c.* Diophtase. The crystals are small, but remarkable in having the primary rhombohedron (polar edges $126^\circ 24'$) predominant at their ends. This rhombohedron exhibits a very distinct striation of its faces parallel to its combination-edges with the accompanying prism of the second order. These diophtases occur in quartz mixed with diophtase.

21. *Albite from the Skopi in the Grisons, and from Viesch in the Valais.*—Principal forms: $0P$, $\infty P\infty$, $P\infty$, $\frac{4}{3}P\infty$, $\infty P'$, $\infty'P$, P ; more rarely $2P\infty$, $2P$, $\frac{4}{3}P$. The albites from the Skopi are mostly intergrown with adularia.

H. W.

"Eklogite" which occurs as Enclosure in the Diamond Mines of Jagersfontein, Orange Republic, South Africa. By E. COHEN (*Jahrb. f. Min.*, 864—869).—The author in support of his original view (*Jahrb. f. Min.*, 1872, 857—861), that the Dry Diggings are crater-like hollows, calls attention to the fact that enclosed masses of stone are found of a nature never before observed in South Africa. One of these masses is about 9 inches in diameter; its surface is rounded in consequence of weathering, as is seen by the numerous protruding sharp edges and angles of crystals. It consists of a white mineral resembling sassurite, light red garnets up to 5 mm. in size, and disthene in bright blue crystals, sometimes 3 mm. long, showing the seldom-observed terminal faces, although not smooth enough for measurement; gold is also present in traces. To determine the nature of this sassurite-like mineral, sections were examined microscopically, but without satisfactory results, since decomposition had spread throughout the mass. Small transparent unaltered particles were left, however, showing well-defined cleavage directions, to which at an angle of 43° (maximum) lies the vibration direction. Small pieces were picked out, quite free from garnets, and probably also from disthene, analysed, and found to have the following composition:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	SrO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.
53.75	13.27	1.19	15.89	0.31	9.92	4.84	0.48	1.09 = 100.74

Hence it would appear to belong to the monosymmetrical pyroxenes. The embedded garnets are always irregular in form, and are always surrounded by a zone of several substances, amongst them plagioclase, and bright green spinelles, which have resulted from the decomposition of the garnets. The disthene (cyanite) crystals are generally free from foreign enclosures, but contain numerous twin-lamellæ. Taking the determination of the pyroxene (viz., omphacite) as correct, the rock is a typical "eklogite," which always occurs enclosed in the older crystalline slates. Such slates occur at a considerable distance to the north of the Diamond Fields, probably extended under them, and afforded material for the filling up of the craters. H. B.

Chemical Composition of Arfvedsonite, and some Allied Minerals. By C DÖLTER (*Zeitschr. f. Kryst.*, 4, 34; *Jahrb. f. Min.*, 1881, 1, Ref. 20).—1. *Arfvedsonite*. The mineral analysed was from Kangerdluarsuk in Greenland, where it occurs, together with felspar and eudialyte, in deeply furrowed crystals without end-faces, and with two cleavage-faces inclined to one another at the hornblende angle; also in cauliform masses. The following table gives the analysis of two varieties, compared with older analyses by Rammelsberg and v. Kobell, which differ considerably in the proportions of ferrous and ferric oxide:—*a.* Rammelsberg; *b.* v. Kobell; *c* and *d.* Dölter: *c*, first variety; *d*, second variety, mean of two analyses:—

	SiO ₂ .	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	MnO.	CaO.	MgO.
<i>a.</i> .	51.22	23.75	7.80	trace	1.12	2.08	0.90
<i>b.</i> .	49.27	14.58	23.00	2.00	0.62	1.50	0.42
<i>c.</i> .	52.22	28.15	5.35	0.64	0.54	2.19	1.45
<i>d.</i> .	49.91	22.83	13.95	1.24	0.42	1.72	0.21

	Na ₂ O.	K ₂ O.	Cl.	Loss by ignition.	
a	10.58	0.68	—	0.16	= 98.29
b	8.00	—	0.24	—	= 99.63
c	10.11	0.34	—	—	= 100.99
d	9.49	0.32	—	—	= 100.09

In calculating the analysis of the first variety, Dölter deducts the K₂O as a constituent of admixed orthoclase, and with this the corresponding quantity (nearly the whole) of the Al₂O₃. He further supposes that the CaO, MgO, and FeO are combined with silica as CaMg₃Si₄O₁₂ and CaFe''₃Si₄O₁₂ (4.5 per cent. of the first, and 11.35 of the second silicate), therefore in the form of tremolite. The remainder consists essentially of the ægirin-silicate, Na₂Fe''₂Si₄O₁₂, present to the amount of 75.33 per cent., leaving a residue of about 5½ per cent., consisting of SiO₂, Fe₂O₃, MnO, FeO, MgO, in successively decreasing quantities. From these calculations the author infers that arfvedsonite consists mainly of the silicate, Na₂Fe''₂Si₄O₁₂, accompanied by CaMg₃Si₄O₁₂ and CaFe''₃Si₄O₁₂ in varying quantities, and small quantities of MgFe''₂Si₄O₁₂, CaFe''₂Si₄O₁₂, and MnFe''₂Si₄O₁₂.

The analysis of the second variety does not agree quite so well with the theory; moreover, the examination of a thin section showed the presence of a foreign mineral. The author, however, infers from a calculation similar to that above detailed, that this arfvedsonite consists mainly of Na₂Al₂Si₄O₁₂, possibly with addition of CaR''₃Si₄O₁₂ and a small percentage of FeSiO₃. Further analyses of pure material are, however, required to establish its exact composition.

2. *Glaucophane*.—This mineral likewise belongs to the amphibole group. The glaucophane of Zermatt consists, according to Bodewig's analysis, half of Na₂Al₂Si₄O₁₂ (as in spodumene), the other half of CaMg₃Si₄O₁₂ (tremolite); CaFe₃Si₄O₁₂, and R''₄Si₄O₁₂ (anthophyllite). A ferric silicate in the residue could not be more exactly determined, on account of uncertainty in the estimation of the ferric oxide.

The glaucophane of Syra gives better results. It consists, according to Lüdecke's analysis, of the silicate Na₂Al₂Si₄O₁₂ (62 per cent.), with a small quantity of the corresponding Na₂Fe''₂Si₄O₁₂, while the residue may be regarded as consisting of the silicates, CaMg₃Si₄O₁₂ and CaFe₃Si₄O₁₂ with excess of FeSiO₃ and MgSiO₃. The chemical analogy of glaucophane to arfvedsonite is therefore evident; both are composed essentially of the silicate, Na₂R''₂Si₄O₁₂, the R'' in glaucophane consisting chiefly of aluminium, in arfvedsonite of iron; both of them also contain a tremolite silicate and an iron silicate, together with excess of an anthophyllite silicate, R''₄Si₄O₁₂.

Gastaldite, which is exactly analogous to glaucophane in constitution, differs from it, according to Cossa's analysis, in containing only 34 per cent. Na₂Al₂Si₄O₁₂, together with larger quantities (about 40 per cent.) of CaMg₃Si₄O₁₂ and Fe₃Si₄O₁₂ (or CaFe₃Si₄O₁₂ and Mg₃Si₄O₁₂) and a silicate, MgAl₃Si₄O₁₂, analogous to the sodium aluminium silicate above mentioned.

3. *Crocodylite*.—The author's analysis of this mineral was made on too small a quantity of material, and is therefore imperfect; it is

however, important, on account of the separation of FeO and Fe_2O_3 , whereas the older analysis by Stromeyer gives only FeO .

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	CaO .	MnO .	Na_2O .	H_2O .
52.22	—	—	34.08	2.48	0.03	0.01	7.07	4.80
52.11	1.01	20.62	16.75	1.77	—	—	6.16	1.58

The water found by Stromeyer was probably due to decomposition. Dölter's analysis shows that crocydolite consists essentially of a sodio-ferric silicate together with ferrous silicate, FeSiO_3 ; that it is in fact a fibrous variety of arfvedsonite. H. W.

Analysis of a Ferruginous Mineral from Amhurst Co., Va.

By A. L. BAKER (*Chem. News*, 42, 194).—This mineral accompanies allanite. It occurs in masses of fibrous structure, has a hardness of 6; sp. gr. 3.32, lustre sub-metallic to silky; colour black; streak reddish-grey. It is moderately fusible before the blowpipe, and gives on analysis:—

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	MgO .	CaO .
37.18	6.29	39.01	3.80	14.10

which gives the formula $(\frac{2}{3}\text{R}'' + \frac{2}{5}\text{Fe}''')(\frac{3}{4}\text{Si} + \frac{1}{8}\text{Al} + \frac{1}{8}\text{Fe}''')\text{O}_3$.

D. B.

Analysis of a Highly Aluminous Pyroxene from Amhurst Co., Va.

By W. T. PAGE (*Chem. News*, 42, 194).—This mineral is found in immediate association with magnetic iron and the allanite occurring in remarkable quantity in the gneissoid rocks of Amhurst Co. It occurs in confusedly crystalline masses, with an approach to foliated structure in some parts and in which the I cleavage can be here and there imperfectly identified. Hardness = fully 6; sp. gr. = 3.420; lustre between vitreous and sub-metallic; colour black; streak ash-grey; translucent only on the edges of their splinters; difficultly fusible before the blowpipe. Analysis gave—

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	MgO .	CaO .
42.50	15.39	11.32	7.50	22.67

These figures lead very closely to the regular meta-silicate formula, counting in most of the aluminium with silicon, the extent of basic and acid replacement being represented pretty nearly by $(\frac{6}{9}\text{R}'' + \frac{2}{9}\text{R}''')(\frac{1}{1} \frac{2}{3}\text{Si} + \frac{1}{15}\text{Al})\text{O}_3$. D. B.

Kentrolite, a New Mineral Species from Chili.

By G. VOM RATH and A. DAMOUR (*Jahrb. f. Min.*, 1881, 1, Ref. 363).—This mineral is a plumbo-manganic silicate, crystallising in the rhombic system. $a : b : c = 0.633 : 1 : 0.784$. Observed forms P , ∞P , $\infty\text{P}\infty$, these faces forming a combination in which the prismatic and pyramidal faces are predominant, and the brachypinacoid is subordinate. Angles $\text{P} : \text{P}$ in the polar edges = $125^\circ 32'$ and $87^\circ 15'$; $\infty\text{P} : \infty\text{P} = 115^\circ 18'$; $\text{P} : \infty\text{P} = 149^\circ 10'$. Cleavage distinct, parallel to the faces ∞P , which are horizontally striated, and have a stronger lustre than the other faces. $\text{H.} = 5$. Sp. gr. 6.19. Colour dark reddish-

brown to blackish. The individual crystals seldom measure more than a few millimeters, but they form groups a centimeter in size, and having the aspect of desmine. The mineral occurs, accompanied by heavy spar, apatite, quartz, and traces of silver bromide, in a breccia-like quartz-vein of Southern Chili.

The mineral heated before the blowpipe with phosphorus salt assumes a faint yellowish colour, which becomes bright violet on addition of nitre. Nitric acid dissolves it partially, leaving manganic oxide. Hydrochloric acid dissolves it, with evolution of chlorine; and on treating the product with the diluted acid, the chlorides of lead and manganese dissolve, and silica remains behind. These reactions show that the mineral must contain either Mn_2O_3 or MnO_2 ; its composition may accordingly be represented as follows:—

	Found.	Calc.			Found.	Calc.
SiO ₂ . . .	15.95	16.21	or	SiO ₂ . . .	15.95	16.58
MnO ₂ . . .	24.50	23.52		Mn ₂ O ₃ . .	22.26	21.83
PbO . . .	59.79	60.27		PbO . . .	59.79	61.59
	100.24	100			98.00	100

The first of these modes of representation leads to the formula $\text{PbO}, \text{MnO}_2, \text{SiO}_2$, the second to $2\text{PbO}, \text{Mn}_2\text{O}_3, \text{SiO}_2$. H. W.

Santorin and its Eruptions. By F. FOUQUE (*Jahrb. f. Min.*, 1880, 2, Ref. 305—319).—The Santorin group of islands in the Grecian Archipelago consists of a peripheric portion formed in prehistoric times, and a central portion which has been produced by repeated eruptions within the limits of authentic history. The more ancient part, comprising the large islands of Thera and Therasia, and the small Island of Aspronisi, forms a nearly circular crater-wall, like that of Somma, composed chiefly of prehistoric eruptive masses, and resting on an old mass of crystalline slates, together with strata of granular limestone, the original nucleus of the entire group. By this ancient nucleus Santorin is geologically marked as a member of the Islands of the Archipelago; and the vast eruptive masses which have been deposited upon it afford, by their oft-repeated alternation of lava-streams and tufa-layers, distinct evidence of a long period of prehistoric activity, resulting in the formation of a large volcanic island, of which Thera, Therasia, and Aspronisi are the circumferential residues.

This island took part in the elevation which occurred in the entire Mediterranean region, after the close of the Miocene age, and at a later date, of which we have no historic record, the central portion sank down, forming the Bay of Santorin, enclosed by the three islands above mentioned. That such a subsidence actually took place is shown by the similar geological structure of the three islands, by the configuration of the sea-bottom, and by the steep declivities of these islands towards the bay. Within the bay formed by this subsidence, there have occurred at later dates, from 179 years B.C. to the present time, fresh outbursts of volcanic activity—analogueous to those which have taken place within the circuit of Somma—giving rise at various epochs, interrupted by long intervals of rest, to the formation of the

Kameni Islands—Palæa-, Nea-, and Micra-Kaméni, and a number of submarine volcanic cones.

The last eruption, which began in January 1866, in the small Bay of Vulcano in Nea-Kaméni, and continued, with various degrees of activity, till October, 1870, was distinguished, especially in its earlier stages, by the emission of actual flames, that is to say, of burning gases, and inflammable gaseous exhalations which took fire on coming in contact with the red-hot lava. The flames emitted between March 21st and April 19th, 1867—an interval of intense volcanic activity—were found by spectroscopic examination to consist of burning hydrogen containing small quantities of chlorine, sodium, and copper.

Palæa-Kaméni, the most westerly of the Kaméni Islands, is 1450 meters long, with a breadth of 400 meters and a height of 93·8 meters at its most elevated point. It is formed mainly of massy or slaty fine-grained lavas, the blistered and glassy varieties occurring less frequently. Chemically and mineralogically these lavas are very nearly related to those thrown out in the eruption of 1866. The dense ground-mass consists chiefly of small fragments of oligoclase and grains of magnetite, with imbedded crystals of labradorite, augite, and magnetite. Tridymite likewise occurs not unfrequently in crystals up to 1 mm. in diameter. Slags, conglomerates, and tufas are of less frequent occurrence. The south-east part of the island consists of a thick bed formed of numerous lava-streams which have flowed over each other, forming plateaux, from which a few lateral streams have flowed in a southerly direction.

Micra-Kaméni, 490 meters long, and 320 meters wide, and of oval shape, had in 1866 a height of 709 meters, but it has since been reduced in height by rather more than a meter. Its southern part is formed of a conical crater, from which a tract formed of lava-streams stretches out towards the north. The lavas of this island are in general compact, almost glassy, of dark brown colour, very seldom scoriaceous. They resemble those of Nea-Kaméni, and those of the eruption of 1866, in outward appearance and in composition, but are distinguished therefrom by their somewhat considerable amount of olivine. The surface of the island is covered to a great extent with light-grey porous angular blocks, partly thrown out in the eruption of 1866.

Nea-Kaméni, before the eruption of 1866, was a scalene triangle with its apex pointing northwards, having a maximum length of 1350 meters, and a breadth of 660 meters. In the south there was a conical crater 106 meters high, reduced to 101 meters by the sinking of the island during the eruption. Its lavas agree perfectly with those of 1866; they are all scoriaceous on the surface and sharp-edged. The southern parts of this island were completely altered in the eruption of 1866, by the addition of lavas and loose ejected masses, which were at first separated from the island, but were gradually joined to it in the course of the eruption. These additions, together with the May islands between the Nea- and Palæa-Kaméni, which were formed at the same time, are included by Fouqué under the collective name of Georgio-Kaméni. The surface of Nea-Kaméni was nearly doubled by these additions, and the conical crater of 1707 was increased by a second cone with several craters, rising to a height of 25 meters above the original crater.

The two submarine cones, Banco and an unnamed cone close to the port of Phira in Thera, have never thrown out lava-streams. All the points of outbreak in the bay of Santorin within the historic era, viz., Palæa-, Mikra-, Nea-, and Georgio-Kaméni, and the submarine cones, are situated on a zone stretching from the shore of Phira in Thera to Aspronisi; that is to say, nearly in a straight line. Santorin has not yet arrived at the formation of a central hollow like Vesuvius or Etna, from which the points of outbreak diverge in radial lines.

The normal lavas of Georgio are augite-andesitic, and contain in a ground-mass having the aspect of obsidian, rather large disseminated crystals of triclinic feldspar, augite, and magnetite. The ground-mass consists of a brown glassy basis, containing numerous microscopic splinters of feldspar; also as accessory minerals, olivine (rarely), hypersthene (frequently), and apatite. By treating the pulverised rock with strong hydrofluoric acid and an electromagnet, Fouqué succeeded in obtaining the constituent minerals of the Georgio lava in a more or less pure state for analysis, and in showing that the disseminated crystals of feldspar consist of labradorite, with a very small quantity of anorthite, and the feldspar splinters of the ground-mass chiefly of albite, perhaps with a little oligoclase. In the ordinary obsidian-like lava there is often found in roundish masses a cubic meter in size, a green lava, consisting of crystals up to 2 mm. long, of anorthite, pyroxene, titanite, olivine, and magnetite, together with variable quantities of a vitreous mass, and drusy aggregates of the same minerals. The results of these separate analyses are given in the following table:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Totals.	Sp. gr.
1.	55·12	29·92	0·35	—	0·79	9·45	5·08	0·08	100·79	2·702
2.	67·58*	18·61	4·91	—	1·73	1·02	5·62	1·33	100·80	2·536
3.	45·93	36·60	0·88	—	1·29	16·09	—	—	100·79	2·762
4.	44·25	37·00	0·43	—	0·07	18·98	0·28	—	101·01	2·756
5.	50·2	3·3	0·4	7·2	12·2	26·4	—	—	99·5	3·372
6.	51·1	3·6	1·0	5·7	13·5	20·4	—	—	100·3	3·358
7.	48·9	7·2	1·3	8·2	6·1	27·8	0·1	—	99·6	3·364
8.	43·6	14·7	—	13·7	5·6	22·8	0·3	—	100·7	3·257
9.	50·1	2·1	1·6	23·6	11·0	10·5	—	—	98·9	3·477
10.	38·17	1·66	—	21·82	35·27	2·90	—	—	99·82	3·603
11.	39·41	2·96	—	13·86	40·60	3·97	—	—	100·80	3·136
12.	59·7	23·2	0·4	—	1·0	7·9	6·6	0·8	99·6	2·629
13.	48·6	6·0	21·13	—	20·0	3·2	trace	—	99·1	3·472
14.	58·4	20·7	8·1	—	2·7	6·2	3·7	0·5	100·3	2·687

1. Labradorite veins of the ordinary Georgio lava. 2. Feldspar splinters in the ground-mass of the same lava, mixed with small quantities of the vitreous basis. 3. Anorthite from the enclosures in the lava-blocks. 4. Anorthite from the druses. 5. Dark-green augite from the normal Georgio lava. 6. Black-green augite from the anor-

* Including 0·51 TiO₂.

thite lava. 7. Black augite from the anorthite druses. 8. Green augite from druses, with a small quantity of anorthite. 9. Brown hypersthene from the ordinary Georgio lava, mixed with a small quantity of augite. 10 and 11. Olivine from the anorthite lava.

Besides the blocks of anorthite lava and the druses of anorthite, the Santorin lavas of 1866 contain nodules of wollastonite, fassaite, and melanite, the analyses of which have been already given in this Journal (1875, 624), and finally roundish lumps from a cubic centimeter to several cubic decimeters in size, having a grey-brown colour, a nearly homogeneous and finely scoriaceous aspect, and closely intergrown with the normal lava. These lumps consist chiefly of triclinic feldspar, with small quantities of light-green augite, yellowish hypersthene, and magnetite, lying in a brown vitreous matrix, interspersed with colourless microliths. The analysis of the plagioclase of these lumps is given under 12 in the preceding table, that of the hypersthene under 13, and the total analysis of the lumps under 14.

The lavas of 1866 were covered in many places with saline deposits. Such a deposit in considerable quantity and of dazzling whiteness was found by Fouqué in 1867 in a fissure of the Aphroessa lava, several meters long, and 35 meters above the sea-level. It consisted of a portion soluble in cold water, and composed chiefly of sodium chloride, with smaller quantities of sodium sulphate and magnesium bicarbonate, and an insoluble portion, composed chiefly of normal magnesium carbonate, mixed here and there with small quantities of basic aluminium sulphate, and traces of ferric oxide and calcium sulphate. It did not contain any bromides, iodides, or potassium salts. This mixture of salts cannot therefore be regarded as a mere deposit left by the evaporation of sea-water. Fouqué endeavours to explain its anomalous composition, according to Gay-Lussac's theory, by the action of sea-water on fused lava. The potassium salts may be supposed to be completely fixed on the lava, while the more abundant sodium and magnesium salts were only partly fixed, the former being volatilised, and carrying with them the magnesia produced by the decomposition of the latter, this magnesia being subsequently converted into chloride and carbonate of magnesium by the action of the fumarole gases.

The ashes yielded by the eruption of 1866 consisted of angular and sharp-edged fragments of very various size, having exactly the composition of the compact rocks. They were evidently formed by disintegration of the lava, which had already attained a highly crystalline structure, and thereby differed essentially from the pumice-like glassy ashes of the prehistoric eruptions occurring in Thera and Therasia. The size of the grains of these ashes and the relative proportions of their constituent minerals were found to depend in great measure on the distance at which they were collected from the point of emission.

The gaseous emanations of Santorin are peculiarly interesting from the fact that, as they are emitted under water, they do not become mixed with atmospheric air, and consequently the combustible gases are not burned at the point of issue: hence the presence of free *hydrogen* in the issuing gases, and the production of flames when it subsequently comes in contact with the red-hot lava, as already men-

tioned (p. 556). In the gaseous exhalations collected between the 28th of March and the 26th of May, 1866, hydrogen was found to play a very conspicuous part, its quantity in the immediate neighbourhood of the eruptive centres amounting to 30 per cent., but decreasing rapidly with increase of distance from the point of issue, also with the decrease of the activity of emission, and of the temperature of the water out of which the gases were collected, the proportion of *marsh-gas* increasing at the same time, and amounting at the maximum to 2.95 per cent. *Hydrogen chloride* was always present in considerable quantity, also *hydrogen sulphide*, the proportion of the latter decreasing with the temperature. *Oxygen* was present in very variable amounts, from 0.20 to 21.56 per cent.

In the spring of 1867 gases were also collected which issued from lava flowing below the surface of the sea. They consisted of carbonic anhydride (traces), oxygen 18 to 26 per cent., nitrogen 72 to 22 per cent., hydrogen 2 to 57 per cent., marsh-gas in varying proportions up to 1 per cent. The flowing lavas therefore contain free oxygen and free hydrogen in a state of absorption, the proportion of hydrogen apparently increasing with the temperature. Hence it would appear that the enormous quantities of water-vapour emitted in volcanic eruptions, exist in the red-hot magma of lava, not as water, but as dissociated hydrogen and oxygen. The gases collected in September, 1875, consisted chiefly of carbonic anhydride (70 to 80 per cent.), with varying quantities of nitrogen and oxygen, and slight traces of marsh-gas and hydrogen sulphide.

The rocks of the more ancient portions of the Santorin Archipelago, Thera, Therasia, and Aspronisi, consist of old mica-slates, with deposits of granular limestones, and of volcanic masses partly of supramarine, partly of submarine origin. In the north of Thera, and in the other islands, the supramarine volcanic rocks predominate, appearing in the form of lava-streams, slags, tufas, pumice, and gangues. The gangues of Northern Thera may be divided, according to their composition, into two groups, all, however, having a vitreous basis, and therefore a porphyritic structure. The ground-mass of the first group contains microscopic splinters of labradorite, magnetite, and augite (often predominant); the glass is always globulitically turbid, and contains disseminated crystals of anorthite, labradorite (subordinate), augite, olivine, apatite, magnetite, and titanite. In the second group the ground-mass contains scarcely anything but albite, oligoclase, and magnetite; augite occurs in small quantity, or is altogether absent; the glass is nearly or quite free from globulites, and therefore clearer than that of the first group; disseminated, there occur labradorite, together with oligoclase and sanidin subordinate, then augite, magnetite, hypersthene, apatite, and here and there isolated crystals of olivine. The second group is therefore more acid than the first, and may be regarded as consisting of typical augite-andesites, whereas the first consists of basalts or of rocks intermediate between these and augite-andesites. The basic group contains, as secondary formations, ferric hydrate, calcite, aragonite, zeolites, and chlorite, whilst the more acid group contains tidymite, which Fouqué supposes to

be formed at the moment of eruption, or shortly afterwards, from the lavas, under the influence of aqueous vapour enclosed therein.

Of special interest is the fact that the pyroxenes in the two groups of lava-rock in Northern Thera are different in composition. In the anorthite-rocks the pyroxenes (all of which are augites) are rich in lime and poor in iron; whereas that of the labradorite-rocks (mixtures of predominant hypersthene with subordinate augite) are poor in lime and rich in iron. The same difference occurs, as appears from the analysis above given (p. 557), in the pyroxenes of the lavas of 1866. From the total analysis of a number of anorthite and labradorite lavas of the district above mentioned, it appears that their ground-mass is always more acid than the separate felspars.

The rocks of the south-west part of Thera (in the neighbourhood of Akrotiri) differ very considerably in composition from those of the north, the more acid rocks predominating, while the true basic ones occur only subordinate.

In the layers of ashes at the foot of the shore-cliffs of Thera and Therasia, especially on the south coast of Thera, are imbedded boulders of granular rocks, which, as nothing like them is to be found in the Santorin Archipelago, must have been loosened and projected from the bottom of the sea. They belong to the older rocks, granites, diorites, &c.

One of the most important formations of the Santorin Archipelago is the layer of pumice which covers a large part of the surface of Thera, Therasia, and Aspronisi, attaining its maximum thickness (30 meters) at Balos on the south-west of Thera, and in the south-west part of Therasia. It consists of alternating layers of lumps and grains of various sizes from fine dust to the size of the fist. Enormous quantities of this pumice are dug out for exportation, so that the layers are splendidly exposed to view. The upper layers contain large numbers of black blocks, consisting of the labradorite rocks found in the north of Thera. More rarely, the pumice-layer contains fragments of anorthite-lava; still more rarely of old crystalline slate. It also contains enclosures of rocks not occurring on Santorin, viz., diabases; also blocks identical in composition with those already mentioned as occurring in the ash-layers of the south-west of Thera; and lastly, blocks of a dark grey porous pyrolitic limestone. The chemical composition of the pumice-glass, freed from crystals and regarded as anhydrous, is as follows:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	TiO ₂ .
71·0	16·8	0·8	0·8	0·7	7·4	2·0	0·5 = 100
H. W.							

Examination of the Iron-meteorite from Rittersgrün. By C. WINKLER (*Jahrb. f. Min.*, 1879, 902—905).—This locality being only a league from Steinbach and Breitenbach, where similar meteorites have been found, renders it probable that all fell at the same time. This meteorite has been mineralogically examined by Weisbach, Breithaupt, and G. Rose, and the author now describes his chemical examination:—It consists of a metallic and a non-metallic

part; the former, sp. gr. = 7·8, consists of nickel-iron and schreibersite; its composition is:—

Fe ₃ Ni.	(FeNi) ₄ P.	Fe ₂ P.	Fe ₂ Si.	FeS.	Cu.
50·406	0·149	0·274	0·169	0·015	0·018 = 51·031 per cent.

of the whole meteorite. The non-metallic part, sp. gr. = 3·12, consists of troïlite, asmanite, bronzite, and chrome-iron.

Troïlite.	Asmanite.	Bronzite.	Chrome-iron.	
7·211	8·527	32·908	0·323	= 48·969 per cent.

of the whole meteorite. The two portions were separated mechanically, by treatment with hydrochloric acid, and by heating in a stream of dry chlorine. The author also proves that asmanite is identical with tridymite, as supposed by Lasaulx. The meteorite contains 1·03 times its volume of a combustible gas. The author supposes in this, and some other cases, that the smooth external crust is due to mechanical abrasion, the light accompanying its fall to the ignition of a combustible gas—the atmosphere of the meteorite, and to the scattering of the dust produced by the abrasion. H. B.

The Meteorite which fell at Estherville, U.S.A., in May, 1879. By J. L. SMITH (*Compt. rend.*, 90, 958).—This meteorite, of which a number of fragments were found, the largest weighing 198 kilos., consists of metallic nodules intermixed with silicates. The mean density is 4·5. A polished surface of the metal shows the Widmanstätt figures very finely developed. The metal gives on analysis:—

Fe.	Ni.	Co.	Cu.	P.
92·00	7·10	0·69	trace	0·112 = 99·902

The other portion of the meteorite consists mainly of bronzite and olivine, with small quantities of chromite, troïlite, and a silicate of undetermined species. The analysis of this last leads to the formula $2\text{SiO}_2, 3\text{RO} = \text{SiO}_2, \text{RO} + \text{SiO}_2, 2\text{RO}$, that is 1 atom bronzite combined with 1 atom of olivine. C. W. W.

Meteoric Dust containing a large Quantity of Metallic Iron, which fell at Catania on the Night of March 29, 1880. By O SILVESTRI (*R. Acc. dei Lincei*, 4, Ser. 3, 1880. Transunti; *Jahrb. f. Min.*, 1881, 1, Ref. 200).—In Sicily, showers of meteoric dust are often observed, sometimes with, sometimes without rain. During such a shower the air becomes murky, and of a reddish-yellow colour; the barometer falls rapidly—10 to 20 mm. from one day to the next; the sea is much agitated by a storm shifting rapidly between north-east and south-east, and a heavy rain leaves a characteristic yellowish-red residue. The dust which fell at the time above-mentioned (bar. 702·5 mm. on March 29th, 752·7 mm. on March 30; thermometer 14·8° on March 29, 16·2° on March 30) contained, in addition to the ordinary constituents (siliceous, calcareous, and argillaceous minerals, and small organisms), particles of metallic iron. It

had a reddish-yellow colour, became black, and gave off an empyreumatic odour when heated, and afterwards recovered its yellowish-red colour. Sp. gr. = 2.92. With strong hydrochloric acid it effervesced strongly, and dissolved to the amount of 25.7 per cent., the solution containing large quantities of the chlorides of calcium and iron. The blowpipe showed the presence of nickel, and phosphoric acid was found to the amount of 0.1456 per cent. P_2O_5 .

Under the microscope small particles of dust were observed, some opaque, others surrounded with a red rim, otherwise steel-grey with metallic lustre. These particles were easily separated by a magnet from the non-metallic more or less transparent particles. The former had a diameter of 0.01 to 0.08 mm.; most of them were irregular, but some were regularly spherical; some also were attached to a transparent vitreous mass. The dust therefore contains nickel-iron, whence it is probably of cosmic origin. The author insists especially on the fact that it did not contain any constituents which might lead to the conclusion that it came from Etna.

H. W.

Analyses of the Waters of the Assiniboine and Red Rivers, Canada. By F. D. ADAMS (*Hoffmann's Chemical Contributions to the Geology of Canada*, Montreal, 1880).—The water of the Assiniboine was taken from the centre of the river, about a quarter of a mile above its junction with the Red River; that of the latter from the middle of the stream, also about a quarter of a mile above the junction of the two. The Assiniboine water, after filtration, had a faint yellowish tinge. The brownish-grey suspended matter, when ignited, left a light, reddish-brown, argillaceous residue. The waters of the Red River, after filtration, had a pale yellowish tinge. The suspended matter was of a light, brownish-yellow colour, and also left an argillaceous residue on ignition. These waters gave on analysis the following results (in grains per imperial gallon):—

	Assiniboine.	Red River.
K_2O	0.499	0.549
Na_2O	5.324	5.028
CaO	6.783	6.912
MgO	4.588	5.142
Al_2O_3 and Fe_2O_3	0.084	0.092
SiO_2	1.571	2.208
SO_3	4.906	7.093
Cl.....	1.988	3.390
Oxygen equiv. to the chlorine ...	0.448	0.765
Total dissolved solid matter dried at 100° C.	41.09	44.63
Suspended matter:—		
Organic.....	0.692	0.342
Mineral.....	4.508	3.509
Total.....	5.200	3.851

Hardness :—

	Assiniboine.	Red River.
Temporary	13.90	16.03
Permanent	6.70	7.87
	<hr/> 20.60	<hr/> 23.90
Specific gravity	1000.64	1000.52

The foregoing acids and bases are probably combined in the water as follows (carbonates being calculated as monocarbonates, and all the salts estimated as anhydrous).

	Assiniboine.	Red River.
Sodium chloride	3.277	5.589
Potassium sulphate ...	0.923	1.015
Sodium „ ...	8.216	4.727
Calcium „ ...	—	6.739
Calcium carbonate	12.112	7.388
Magnesium carbonate .	9.635	10.798

The analysis of the Assiniboine water gives an excess of soda above the amount required for the sulphuric acid, amounting to 0.114 gram (= 0.084 Na); this might be present as carbonate; it would require 0.129 chlorine, or 0.147 sulphuric acid in excess of the amounts found of those respective constituents; it has been calculated as sodium sulphate and added thereto.

H. W.

The Hot Springs of the Littoral Chain of Venezuela. By BOUSSINGAULT (*Ann. Chem. Phys.* [5], 22, 145—152).—The littoral chain extends towards the west from the hills of Avila to Nueva Valencia, where it joins an eastern branch of the Andes. The mountains are mainly composed of granite and gneiss, and abound in hot springs. The following table gives the peculiarities of the most important of them :—

Name of spring.	Altitude.	Temperature.	Sulphates and chlorides.	Odour.	Residue.	Gas evolved.
I. Onoto.....	feet. 2281.9	44.5° (air in shade 30°).	None.	None.	Very small, with alkaline reaction.	Nitrogen (occasionally).
II. Mariara	1813.1	36—60°	Traces.	H ₂ S (slight).	Siliceous. Alkaline.	Nitrogen (frequently).
III. Las Trincheras.	1065.5	92—96.9°	Small quantities.	H ₂ S (strong).	Siliceous. Alkaline.	Nitrogen (occasionally).

The temperature of the springs appears to vary with their altitude. The decrease is about 1° for every 21 feet of ascent.

The plant called by Vandelli *Ulva labyrinthiforma*, is found in the Mariara spring. The following is an analysis of the Las Trincheras water :—

	Gr.		Gr.
1 litre contains :			
Chlorine	0·058	Lithia	traces
Sulphuric acid	0·034	Silica	0·127
Boric acid	0·000	Oxide of iron	0·012
Soda	0·066	H ₂ S and CO ₂	—
Potash	0·014	Oxide of copper	0·000
Lime	0·013	Arsenic	0·000
Magnesia	0·006	J. I. W.	

Water from a Hot Spring, New Britain. By A. LIVERSIDGE (*Chem. News*, 42, 324).—The water is of a yellow tinge, and smells of sulphuretted hydrogen. At first, it is neutral to test-paper, but afterwards becomes very faintly acid, probably from the oxidation in part of the sulphuretted hydrogen. No attempt was made to determine the amount of the latter and other gases. The residue left on evaporation to dryness at 100° C. amounted to 36,312 parts per 1,000,000, or 2541·84 grains per gallon, which is about the same as average sea-water.

The following is the composition of the residue dried at 100°:—

	Per cent. in residue.	Parts per million of water.	Grains or per gallon.
Silica	0·200	72·6	5·08
Alumina and iron oxide . .	0·440	159·7	11·18
Calcium sulphate	1·394	506·2	35·43
Calcium chloride	2·240	813·4	56·93
Magnesium chloride	4·710	1710·3	119·72
Sodium chloride	87·320	31707·6	2219·53
Potassium	traces	—	—
Combined water	3·696	1342·2	93·97
	<hr/> 100·000	<hr/> 36312·0	<hr/> 2541·84

D. B.

Water from a Hot Spring, Fiji Islands. By A. LIVERSIDGE (*Chem. News*, 42, 324).—The water is clear and colourless, after the deposition of a small amount of matter, which it had in suspension, free from smell, but with a strongly marked saline taste, and faintly alkaline or almost neutral to test-papers. Its specific gravity is 1·0064. The total quantity of solid matter in solution dried at 110° gave 8·320 parts per million, or 582·40 grains per gallon, consisting of—

	Per cent. in residue.	Parts per million of water,	Grains or per gallon.
Silica, insoluble	1·681	133·3	9·20
Silica, soluble	0·074	5·8	0·40
Alumina and traces of ferric oxide	0·534	41·7	2·92
Aluminium chloride	1·646	128·6	9·00
Phosphoric acid (P_2O_5)	traces	—	—
Calcium chloride	46·754	3652·9	255·70
Calcium sulphate	4·770	372·7	26·09
Magnesium chloride	0·154	12·0	0·84
Sodium chloride	42·171	3294·8	230·64
Potassium chloride	1·756	137·2	9·60
Carbonic acid	traces	—	—
Loss	0·460	34·0	2·52
	100·000	7813·0	546·91
			D. B.

Organic Chemistry.

Ethane. By J. THOMSEN (*J. pr. Chem.* [2], **23**, 163—166).—Differences between the heat of combustion found by Berthelot in the case of ethane produced electrolytically from sodium acetate, and by Thomsen in that of ethane obtained from zinc ethide and hydrochloric acid, led Thomsen to the conclusion that a real difference existed between dimethyl and ethyl hydride; that is to say, that ethane existed in two isomeric conditions. The author has now very carefully determined the heat of combustion of the two ethanes, and finds that Berthelot's figure is somewhat too high, and that the heat of combustion of the two bodies is absolutely the same, and that they must therefore be considered as identical. O. H.

Dipropargyl. By L. HENRY (*Ber.*, **14**, 399—403).—Dipropargyl combines directly with iodine to form the tetriodide $C_6H_6I_4$ (m. p. 113°). This compound is best prepared by the addition of a solution of iodine in potassium iodide to dipropargyl; the crystalline precipitate produced is recrystallised from carbon bisulphide, from which it is deposited in quadratic prisms, resembling hippuric acid in appearance. The crystals are sparingly soluble in ether and alcohol, and are decomposed by alcoholic potash. The formation of dipropargyl by the action of alcoholic potash on diallyl dibromide takes place in two stages, diallylene monobromide being the intermediate product. This body is a colourless liquid (b. p. about 150°), insoluble in water. It forms characteristic precipitates with ammoniacal copper and silver solutions.

In the purification of dipropargyl by distilling its cuprous compound with hydrochloric acid, a polymeride, crystallising in glistening plates (m. p. 100°), is obtained as a bye-product. W. C. W.

Formation of Chloroform from Alcohol and Bleaching Powder. By A. BÉCHAMP (*Ann. Chim. Phys.* [5], 22, 347—353).—The formation of chloroform when a mixture of alcohol and bleaching powder is gently heated, has been explained in various ways by different chemists, some of whom have attributed the frothing which accompanies the reaction to the evolution of carbonic anhydride. The author has found that the gas which is given off contains no carbonic anhydride, but consists of almost pure oxygen, either a product of the same reaction which produces the chloroform, or of a peculiar decomposition of the hypochlorite. According to Dumas, aldehyde C_2H_4O is first formed by the dehydrogenation of the alcohol, and this by substitution gives rise to chloral, which is converted by the action of the calcium hydrate into chloroform. These changes may be brought about in two ways. The hypochlorous acid may split up into oxygen, which is given off, and chlorine, which first abstracts hydrogen from the alcohol and then forms chloral by substitution. It is, however, difficult to explain this decomposition of the hypochlorous acid, and also how the chlorine could act on the alcohol in presence of a large quantity of calcium hydrate. On the other hand, the alcohol may be attacked by the hypochlorous acid as a whole, thus: (1) $2C_2H_5O + CaCl_2O_2 = 2C_2H_4O + H_2O + 2HCl + CaO = 2C_2H_4O + 2H_2O + CaCl_2$. (2) $2C_2H_4O + 3CaCl_2O_2 = 3CaH_2O_2 + 2C_2HCl_3O$. (3) $2C_2HCl_3O + CaH_2O_2 = 2CHCl_3 + Ca(HCO_2)_2$. This theory assumes that in the reaction which produces the chloroform, no gas is given off. If the formic acid were oxidised to carbonic anhydride, the latter would be formed in presence of a quantity of calcium hydrate more than sufficient to combine with it.

100 grams bleaching powder, 50 grams calcium hydrate, and 400 c.c. water were heated to 80° , and 15 grams chloroform, the quantity which the mixture would have produced with alcohol, were added. The mixture at once swelled up and the chloroform distilled over. During the distillation no gas was given off, but when the whole of the chloroform had passed over and the temperature of the residual liquid was raised to ebullition, oxygen gas, free from carbonic anhydride, was evolved, and the liquid acquired a rose colour, owing to the formation of a small quantity of permanganic acid, due to the presence of manganese in the lime. Oxygen was also given off when a similar mixture was heated to ebullition without addition of chloroform, and also when 100 grams bleaching powder and 400 c.c. water were heated without addition of calcium hydrate; in both cases a small quantity of permanganic acid was formed. 100 grams bleaching powder, 50 grams calcium hydrate, and 400 c.c. water were heated to 80° , and 16 grams alcohol at 90° were added; the mixture immediately frothed up. At first no gas was evolved, but when all the chloroform had distilled over and the temperature was raised, pure oxygen gas was given off in large quantity; no permanganic acid was formed. Even if the bleaching powder and water were not mixed with calcium hydrate, no carbonic anhydride was given off. These experiments confirm the second of the two theories given above. The chloroform is produced without evolution of gas, the oxygen which is given off being the result of the decomposition of the hypochlorite.

The frothing is due to the production of the chloroform in a medium the temperature of which is higher than its boiling point.

C. H. B.

Conversion of Normal into Isopropyl Bromide by Heat. By L. ARONSTEIN (*Ber.*, **14**, 607—609).—If the author's view is correct (*see* p. 576), that ethyl bromide is decomposed into ethylene and hydrobromic acid, propyl bromide should in the same way decompose into propylene and hydrobromic acid. On the recombination of the hydrobromic acid with the propylene, *iso* and not *normal* propyl bromide should be formed. The author has succeeded, by heating it at 280°, in partially converting normal into isopropyl bromide, which was identified by its boiling point, the formation of isopropyl benzoate and of acetone. From these results, the author considers it not improbable that in the conversion of calcium cumate into cumene there is a conversion of a normal into an isopropyl group, a change which he proposes to investigate.

V. H. V.

Allyl Iodide and Monobromallyl Alcohol. By L. HENRY (*Ber.*, **14**, 403—405).—The irritating odours which are observed in the preparation of allyl iodide by the action of phosphorus and iodine on glycerol are due to the presence of allyl alcohol. The author considers it probable that di-iodhydrin, $C_3H_5(OH)I_2$, is formed in the first instance, and afterwards splits up into iodine and allyl alcohol, and that the alcohol is then converted into allyl iodide by the action of phosphorus and iodine.

Monobromallyl bromide (b. p. 152°), prepared by treating tri-bromhydrin (b. p. 142°) with sodium, is converted into *monobromallyl alcohol*, $C_3H_4Br.OH$, when heated in sealed tubes at 130° with water. An aqueous solution of potash removes the bromine from monobromallyl alcohol, converting it into propargyl alcohol. W. C. W.

The Saccharoses. By BERTHELOT (*Ann. Chem. Phys.* [5], **22**, 287—288).—The author points out the resemblance which Péligot's saccharin bears to trehalose. Measurements of the angles of crystals of both substances give almost identical values. They are both more stable than the other saccharoses, and neither of them is attacked by dilute sulphuric acid. The author mentions that twenty years ago he predicted in his *Chimie Organique fondée sur la Synthèse* the preparation of this class of substances.

J. I. W.

Maltose. By E. KÜLZ (*Pflüger's Archiv*, **24**, 81—84).—The author states that at the time that Musculus and v. Mering published their paper "On the Changes produced in Starch and Glycogen by Diastase, Saliva, Pancreas, and Liver-ferment," he had been engaged for three years in the investigation of the subject. He prepared two samples of glycogen-maltose, which yielded, on analysis, results as follows:—

	Found.		Calculated for the formula
	I.	II.	$C_{12}H_{22}O_{11} + H_2O.$
C. . .	39.62	39.42	40.0
H ..	6.76	6.72	6.67

From these figures and the comparisons of their rotations, he considers the identity of maltose prepared from glycogen and from starch proved, and states that his experience shows that the usual products of the action of the ferments above-mentioned are achroodextrin and maltose, with occasional traces of grape-sugar, probably a secondary product.

W. N.

Maltose. By H. YOSHIDA (*Chem. News*, **43**, 29—31).—The maltose employed was extracted from *amé* (a substance used in Japan as a sweetmeat and for some other purposes), in which it is present to the extent of 45 to 75 per cent. Its specific rotatory power, determined by means of a Soleil-Ventzky saccharimeter, was 150·25, and its reducing action on cupric oxide, estimated by means of Fehling's solution, was 61·01, a number which agrees with that given by Brown and Heron, 60·8; O'Sullivan found 65. Experiments with Dr. Pavy's method, using different quantities of ammonia in preparing the copper solution, showed that the reducing power of the maltose is largely influenced by the proportion of ammonia present. The ratio 1 : 5 for dextrose and cupric oxide was obtained only when the exact quantity of ammonia recommended by Dr. Pavy was used. The reducing action of dextrose is much more rapid than that of maltose, and is affected to a greater extent by the proportion of ammonia employed.

When oxidised by nitric acid, maltose gives saccharic acid, and, like cane-sugar and dextrose, when treated with chlorine in presence of water, it yields gluconic acid. Oxidation with potassium permanganate gave no definite results. When 2 parts maltose, 1 part acetic anhydride, and 5 parts glacial acetic acid are heated at 110°, a dark-coloured mass is obtained, which contains, besides other bodies not examined, a light yellow solid substance which is insoluble in ether, reduces Fehling's solution, has a taste at first sweet, but afterwards bitter, and is in all probability the monacetyl-derivative of maltose, $C_{12}H_{21}O_{11}\bar{A}c$.

C. H. B.

Remarks on some Experiments with Maltose. By J. STEINER (*Chem. News*, **43**, 54).—Referring to Yoshida's paper (preceding Abstract), the author mentions that the specific rotatory power of maltose, if calculated from the appended analytical data, is not $[\alpha]_D = 150\cdot25$, but less. Soleil-Ventzky's saccharimeter was used, and the number of angular degrees corresponding to 100 divisions on the scale of this instrument is not 39·61, as introduced in the calculations, but 39·1 for 100 divisions; this number has to be taken into account when the specific rotatory power for the transition tint $[\alpha]_D$ is to be calculated for. No mention is made about the water of hydration of maltose crystals, although it is known that maltose crystallises with 1 mol. H_2O , corresponding to an increase in weight of 5 per cent. Another important point which Yoshida seems to have disregarded is, that maltose solutions have the peculiar property of "by-rotation," similarly as is the case with dextrose. The result of the "CuO" reducing power of maltose proves that he worked with the crystals, as he obtained the number 61; while the proportion $95 : 100 = 61 : (x = 64\cdot2)$ shows the

CuO reducing power for anhydrous maltose $k = 64.2$, agreeing with the value given for anhydrous maltose by O'Sullivan. D. B.

Elementary Composition of Glycogen. By E. KÜLZ and A. BORNTÄGER (*Pflüger's Archiv*, **24**, 19—27).—The results of the analyses by a large number of investigators are quoted both of glycogen (*sic*) and compounds of glycogen with lead and barium; these tend to show that about 44.5 per cent. C, and about 6.5 per cent. H, represents the composition of glycogen. A table showing the results of analyses of glycogen from various sources by the author is given, together with details of the method of preparation; the mean obtained was 43.61 per cent C, and 6.45 per cent. H, which satisfy the formula $6(C_6H_{10}O_5) + H_2O$, and are almost precisely the figures obtained by Nägeli for amyloextrin, dried at 100° . On drying at 110° slightly different figures were obtained, which, according to the authors, indicate the possibility of another formula. W. N.

Specific Rotatory Power of Glycogen. By E. KÜLZ (*Pflüger's Archiv*, **24**, 85—90).—After quoting the figures given by numerous observers, the author gives a table of the results of his own experiments with glycogen, prepared with great care from various sources, and on various diets; they vary from 203° to 233.5° , the mean agreeing fairly with that obtained by Böhm and Hoffmann. Attention is drawn to the errors likely to be introduced in the process of preparation, and the difficulty of obtaining a perfectly pure sample. A table is given which shows that dilution of the solution tends to raise the readings very considerably. W. N.

Action of Mineral Acids on Glycogen. By E. KÜLZ and A. BORNTÄGER (*Pflüger's Archiv*, **24**, 28—41).—It has always been assumed that glycogen, when treated with dilute mineral acids, was converted into grape-sugar, but no detailed proof that such is the case has yet been given. The authors have therefore investigated the matter as follows:—

20 grams of very carefully prepared glycogen from horse's liver was treated with 400 c.c. water and 60 c.c. dilute sulphuric acid (1 part concentrated acid in 5 of water) in a flask with a condenser attached for 7 hours on a water-bath heated to boiling. The sulphuric acid was then removed by means of barium carbonate, afterwards by baryta-water, and the neutral filtrate evaporated to a syrup and treated with boiling alcohol. This solution would not crystallise, but on removing a portion, driving off the alcohol, and returning the residue to the original solution, an abundant formation of crystals ensued.

These gave the following results:—

1. Both to the naked eye and under the microscope their appearance agreed exactly with that of grape-sugar.

2. 0.9440 gram of the substance (air-dried) gave 0.0035 gram ash.

3. A concentrated aqueous solution, when treated with ten times its volume of 99.5 per cent. alcohol, gave no precipitate. There was therefore no dextrin present.

4. Barford's reagent in aqueous solution gave rapid reduction.

5. The freshly prepared aqueous solution exhibited a rotation (6 per cent.), which on boiling and subsequent cooling for 24 hours, was reduced one-half (3 per cent.).

6. An aqueous solution after standing 24 hours, gave by rotation 1 per cent., and by Fehling's method, 1.0169 per cent. grape-sugar.

7. Elementary analysis gave—

	Calculated as $C_6H_{12}O_6 + H_2O$.	Found.
C	36.36 per cent.	36.51 per cent.
H	7.07 „	6.96 „

An investigation of the compounds of the sugar obtained from glycogen with sodium chloride, showed precisely the same results as the compound of sodium chloride and grape-sugar. There is therefore no doubt that the sugar obtained by the action of dilute mineral acids on glycogen is identical with grape-sugar.

The merits of various methods of conversion are then discussed at great length, and a table of results given, which tend to show that the methods of Fresenius, Will, and Sachsse are the best. W. N.

Schtscherbakoff's A, B, C, and D Glycogen. By E. KÜLZ (*Pflüger's Archiv*, 24, 94—97).—The author is of opinion that these bodies, described by Schtscherbakoff (*Ber.* 1870, 200), are not different forms of glycogen, but glycogen derivatives. W. N.

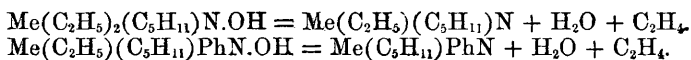
Conversion of Glucose into Dextrin. By F. MUSCULUS and A. MEYER (*Bull. Soc. Chim.* [2], 368—371).—On adding to 20 grams of glucose 30 grams sulphuric acid, stirring the mixture constantly, heating it at 60° until it becomes brown, and then throwing it into 800 grams absolute alcohol, there is formed, in about a week, a thick precipitate, consisting of a white hygroscopic powder of the composition $C_{16}H_{28}O_{14}$, C_2H_6O . On boiling with water the alcohol is eliminated, and water substituted. A yellow amorphous mass is thus obtained, having all the properties of dextrin, $C_{18}H_{28}O_{14}$, $H_2O = 3(C_6O_{10}O_5)$. It is not fermented by yeast or converted into sugar by diastase. After boiling for some time with acidulated water (4 per cent. H_2SO_4), it is converted into glucose. Its diffusibility as tested by dialysis is less than that of the sugars, but greater than that of the natural dextrins.

L. T. O'S.

Erythrodextrin. By F. MUSCULUS and A. MEYER (*Zeits. f. Physiol. Chem.*, 4, 451).—According to Musculus and Nägeli it is a soluble starch, which gives with iodine not a blue but a red reaction; possibly the so-called erythrodextrin may be a mixture of achroodextrin and soluble starch. The authors obtained the intense red colour which characterises erythrodextrin, when a half per cent. solution of soluble starch was added to a solution of a higher dextrin which gave a pure yellow-brown reaction with iodine. W. N.

Action of Heat on the Ammonium Bases. By A. W. HOFMANN (*Ber.*, 14, 494—496).—When an ammonium hydroxide containing

different alcoholic radicles is decomposed by heat, the tertiary base which is formed will contain the radical methyl, if the original hydroxide contained the methyl-group. One of the other groups is liberated in the form of a hydrocarbon, *e.g.*, methyldiethylamyl ammonium hydroxide splits up into methylethylamine and ethylene, whilst methylethylamylphenylammonium hydroxide forms methylamylphenylamine and ethylene.



Dimethylpiperylammonium hydroxide yields trimethylamine and the hydrocarbon C_6H_8 . The conine derivative under similar treatment forms trimethylamine and the hydrocarbon C_8H_{14} . W. C. W.

Ethylhydroxylamine and Vapour-density Determinations of a few Hydroxylamine Derivatives By O. GÜRKE (*Annalen*, **205**, 273—278).—Both ethylic ethylbenzoylhydroxamate and the ethylhydroxylamine derived from it were found to be volatile without decomposition.

Ethylic ethylbenzoylhydroxamate, $\text{N}\bar{\text{B}}\text{zEtO}$.—Sp. gr. 1.0258 at 17° . It boils at 244° (755 mm.) with slight decomposition, an odour of phenyl cyanate being produced, and a small quantity of a solid separated. The vapour-density by Hofmann's method was 6.56 (theory, 6.68). Ethylic ethylbenzoylhydroxamate is decomposed by long heating at 270° in sealed tubes. Ethylic ethylbenzoylhydroxamate is metameric with ethylphenylurethane (b. p. $245\text{--}250^\circ$), but is not changed into it by distillation.

Ethylhydroxylamine.—The hydrochloride may be obtained in the crystalline state by saturating moist ether with hydrochloric acid, and heating it with ethylic ethylbenzoylhydroxamate. The solution cannot be evaporated without decomposition; it melts at 128° . By heating it in sealed tubes with hydrochloric acid (sp. gr. 1.14) at 150° , ethyl chloride and hydroxylamine chloride are produced, the latter being decomposed with formation of ammonium chloride at a higher temperature.

Ethylhydroxylamine hydrochloride is decomposed on dry distillation, giving off hydrochloric acid and combustible gases, and leaving a residue of ammonium chloride, but ethylamine is not formed. The *acid sulphate*, $\text{NHEt.HO.H}_2\text{SO}_4$, obtained from the hydrochloride by means of silver sulphate, evaporation, and drying over sulphuric acid, is very readily soluble, both in water and absolute alcohol, and crystallises with great difficulty. The *acid oxalate*, $\text{NHEt.HO.C}_2\text{H}_2\text{O}_4$, from the hydrochloride by silver oxalate, evaporation, solution of residue in absolute alcohol, and precipitation by ether: colourless powder. The nitrate could not be obtained crystallised. *Ethylhydroxylamine*, NHEt.HO . A concentrated solution of the hydrochloride is decomposed by the equivalent quantity of potash, and the vapours are passed through a tube containing solid potash, at about 80° , the distillate being condensed in a well-cooled receiver. For complete dehydration the base is again distilled over solid potash. It is a transparent, highly mobile, combustible fluid, with a strong odour, different from that of

ammonia, alkaline reaction, and miscible with water, alcohol, and ether in all proportions. It distils with steam or alcohol vapour; boils at 68° . Sp. gr. 0.8827 at 7.5° . Sodium has at first no action on ethylhydroxylamine, but the liquid soon becomes warm, ammonia is copiously evolved, and the metal is changed to a white pulverulent mass, readily soluble in water to an alkaline liquid. It contains carbon, hydrogen, and nitrogen, in addition to sodium.

The reactions of ethylhydroxylamine solutions with *silver nitrate*, *mercuric chloride*, and *cupric sulphate* are given. The statement of Lossen and Zanni (*Annalen*, **182**, 223) that silver, mercury, and copper salts are reduced by ethylhydroxylamine in alkaline solutions is correct only for silver salts; the author attributes this discrepancy to the presence of hydroxylamine. By the action of benzoic chloride on ethylhydroxylamine, the ethylbenzoylhydroxamate of Waldstein (*Annalen*, **181**, 384) is produced.

F. L. T.

Bases of the Oxalic Series. By O. WALLACH and E. SCHULZE (*Ber.*, **14**, 420—428).—In the preparation of the propylamine, used for building up the higher members of this series, better results were obtained by the action of alcoholic ammonia on propyl nitrate than on the chloride. The nitric acid (sp. gr. 1.4) used in the preparation of the nitrate, is boiled with 0.6 per cent. of urea, and a current of air is blown through the hot acid for a few seconds: 25 grams of this acid are brought into a flask of 200 c.c. capacity, which is provided with a condenser; 15 grams of propyl alcohol, 3 grams of urea and some talc are then added, and the mixture heated to 95° . A fresh quantity (equal volumes) of acid and alcohol is poured into the flask, and the liquid boiled until its temperature reaches 105° , when acid and alcohol are again added. On washing the distillate with water, the nitrates separate as a heavy liquid. Normal propyl nitrate boils at 110.5° , and isopropyl nitrate boils at 101° . The nitrate is converted into propylamine by heating at 100° , with a 10 per cent. solution of alcoholic ammonia. Dipropylamide, obtained from propylamine, melts at 162° .

The following oxalines have been prepared:—

Chloroxalmethylamine, $C_4H_5ClN_2$, from dimethylamide (m. p. 210°), boils at 205° , and has a sp. gr. of 1.2473 at 16° . The hydriodide, crystallising in transparent needles soluble in water and alcohol, is decomposed by phosphorus and iodine, forming *oxalmethylamine*, $C_4H_6N_2$, a liquid (b. p. 197°) miscible with water. The platinochloride, $(C_4H_6N_2.HCl)_2.PtCl_4$, crystallises in prisms, which are sparingly soluble in cold water. The zincochloride, $(C_4H_6N_2.HCl)_2.ZnCl_2$, forms anhydrous prisms (m. p. 128°), soluble in alcohol and water. The salt is reprecipitated from the alcoholic solution by the addition of ether. The base combines with methyl iodide, to form the methiodide $C_4H_6N_2.MeI$. If an aqueous solution of this compound is treated with silver chloride, and the product mixed with platinum chloride, rhombic plates are deposited, which have the composition $(C_4H_6N_2.MeCl)_2.PtCl_4$.

Oxalpropylamine, $C_6H_{14}N_2$, prepared from chloroxalpropylamine (b. p. 236°), is an oily liquid, miscible with water (b. p. 230° , sp. gr. 0.952 at 17°). The methiodide, $C_6H_{14}N_2.MeI$, is soluble in water and melts without decomposition. The platinochloride, $(C_6H_{14}N_2.MeCl)_2.PtCl_4$, crystallises

in plates, and the zincchloride, $(C_6H_{14}N_2, HCl)_2, ZnCl_2$, in prisms (m. p. 92°). On heating a mixture of lime and chloroxalethylene or oxalethylene zincchloride, ethylene, pyrroline, and a new base, $C_4H_6N_2$ (m. p. 136° , b. p. 267°), are formed. Oxalmethyline gives similar results, but oxalpropylene appears to yield a new base (b. p. $250-255^\circ$).
W. C. W.

Action of Furfuraldehyde on Aldehydes and Acetone in presence of Soda. By J. G. SCHMIDT (*Ber.*, **14**, 574—576).—By heating together furfuraldehyde and propaldehyde with a 10 per cent. soda solution to $20-30^\circ$, furfurcrotonic aldehyde is obtained as a golden, strongly refractive, cinnamon-smelling oil thus: $C_4H_3O.CHO + CH_3.CH_2.CHO = H_2O + C_6H_8O_2$. This aldehyde cannot be distilled without decomposition; with fuchsine sulphite it gives a golden colour, which immediately turns violet; with aniline and acetic acid it gives a green colour; it resembles in its reactions its homologue, furfuracrolein. By silver oxide, the aldehyde is oxidised into the corresponding acid, $C_8H_8O_2$, which forms slender needles melting at 107° .

Benzaldehyde and furfuraldehyde, with soda solution, gave no characteristic reaction. Acetone and furfuraldehyde react to form a substance, crystallising in long white needles (m. p. 37°), which the author is at present investigating.
V. H. V.

The Vapour of Chloral Hydrate. By L. TROOST (*Ann. Chem. Phys.* [5], **22**, 152—170).—In a previous paper, the author described his experiments on the vapour of chloral hydrate at the temperatures of 100° and 79° . The present memoir contains an account of those made at 60° . The apparatus employed by the author consists of a glass cylinder of 1 litre capacity, one end of which is drawn out to a capillary tube, the other is fused on to a piece of barometer tubing. The whole is encased in an outer tube, through which circulates the vapour of chloroform. Before commencing the experiment the pressure in the cylinder is reduced to 2—3 mm. by means of a Sprengel pump attached to the capillary tube, which is then sealed up. A small quantity of neutral anhydrous potassium oxalate is introduced into the apparatus through the barometer tube, and the level of the mercury read off. Then a weighed quantity of chloral hydrate is added, and the second reading made. The level of the mercury is also noted occasionally during the following 20 hours.

By employing hydrated neutral potassium oxalate, the author shows that the presence of free water decreases the pressure.

If the chloral hydrate has a definite composition in the state of vapour, the addition of anhydrous potassium oxalate ought not to cause a diminution of pressure. The following are the results obtained by the author:—

I. Using anhydrous oxalate:—

Weight of chloral hydrate employed.....	Gram. 0.245
---	----------------

	Mm.
Obs. pressure after the introduction of chloral hydrate	71·8
„ „ 4 hours	71·2
„ „ 12 „	71·2
„ „ 15 „	71·3
„ „ 19 „	71·2
„ „ 22 „	71·4

II. Using hydrated oxalate :—

	Gram.
Weight of vapour of water introduced.....	0·0265
	Mm.
Sum of the calculated pressures after introduction of water	72·6
Pressure observed after the introduction of water....	71·7
„ 2 hours 30 minutes after introduction of water	70·0
„ 9 hours after the introduction of water	68·3
„ 17 hours after the introduction of water.....	66·5
„ 24 hours after the introduction of water	65·4

It is therefore evident that at a temperature of 60° chloral hydrate exists as vapour.

The author discusses at length the experiment made by Wurtz, and states that the hygrometric method is not trustworthy at the temperature and pressure at which this chemist worked. He finds that a slight chemical action takes place between the potassium oxalate and chloral hydrate, in which potassium chloride is formed. He also refers to another experiment performed by Wurtz, in which he took two Hofmann's tubes, one containing vapour of chloroform, the other chloral hydrate, at 100°, and introduced a small quantity of potassium oxalate into each, when the level of the mercury in the second one fell, that in the other remaining constant. The author has shown that chloral hydrate decomposes at 100°, and therefore the tube contained free aqueous vapour.

J. I. W.

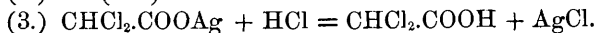
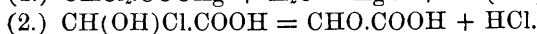
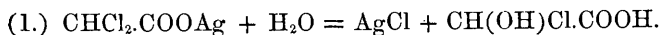
Action of Heat and Water on the Halogen-substituted Acids of $C_nH_{2n}O_2$ Series. By H. BECKURTS and R. OTTO (*Ber.*, 14, 576—591).—This paper is a continuation of the author's former researches on the decomposition of halogen acids of the acetic acid series.

Silver monochloracetate.—This salt, when heated with a quantity of water insufficient for its solution, is easily converted into glycollic acid. When it is heated in the dry state to 70—80°, it is decomposed into silver chloride and glycolide, $CH_2Cl.COOAg = AgCl + CH_2O.CO$.

Silver dichloracetate.—The authors allude to the different results obtained by former experimenters on the action of water on silver

dibromacetate. When silver dichloracetate is heated with a quantity of water insufficient for its solution, there are formed, besides silver chloride, almost equivalent quantities of glyoxylic acid and regenerated dichloracetic acid. This result is in accordance with Perkin's experiments (this Journal, 1879 [2], 90) on silver dibromacetate. Debus (*Annalen*, **100**, 1) has described potassium glyoxylate as deliquescent, the authors, however, find that the salt, when pure, is perfectly stable.

The authors explain the reaction thus: by the action of water on silver dichloracetate, silver chloride and monochloroglycollic acid are formed. The latter is readily decomposed into glyoxylic and hydrochloric acids, which in its turn reacts with the unaltered silver dichloracetate to form dichloracetic acid and silver chloride:—



The authors have repeated Perkin and Dnppa's researches on silver dibromacetate, and find that it is similarly decomposed into silver bromide, glyoxylic and dibromacetic acids.

Calcium glyoxylate.—On neutralising an alcoholic solution of glyoxylic acid with calcium carbonate, the author obtained a gelatinous calcium glyoxylate, which in drying became compact and crystalline. Its composition is expressed by a formula $(\text{C}_2\text{HO}_3)_2\text{Ca}_4\text{H}_2\text{O}$, or $(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, whilst ordinary calcium glyoxylate has the constitution $(\text{C}_2\text{HO}_3)_2\text{Ca}$. From a dilute solution of this anomalous salt, the ordinary salt can be crystallised out, the change within the liquid being perfectly visible.

Calcium dichloracetate crystallises from hot water and alcohol in small anhydrous needles, but from aqueous alcohol with 3 mols. H_2O .

When dry silver dichloracetate is heated by itself, it is decomposed into silver chloride, and a substance, which is probably a mixed anhydride of dichloracetic and glyoxylic acids, $2\text{CHCl}_2.\text{COOAg} = 2\text{AgCl} + \text{CHCl}_2.\text{CO}.\text{O}.\text{CO}.\text{CHO}$. The anhydride, however, cannot be separated by distillation from the silver chloride, for it is decomposed into dichloracetic and carbonic acids, but it may be converted by cold alcohol into ethyl dichloracetate. The anhydride was not isolated by Friedrich (*Annalen*, **206**, 254) in the distillation of potassium dichloracetate, but this is probably due to the fact that the potassium salt requires a far higher temperature for its decomposition, and the change is never so complete.

Silver trichloracetate.—When this salt is heated with water, chloroform, carbonic anhydride, carbonic oxide, and trichloracetic acid are formed. The reaction can be explained by supposing that an intermediate dichloroglycollic acid is formed, which is decomposed into hydrochloric acid, carbonic anhydride, and carbonic oxide; the hydrochloric acid then reacts with the undecomposed silver trichloracetate to form trichloracetic acid, which is partly decomposed into chloroform and carbonic anhydride. Dry silver trichloracetate is decomposed into silver chloride, carbonic anhydride, and oxide, and trichloracetic anhydride $3\text{CCl}_3.\text{COOAg} = (\text{CCl}_3.\text{CO})_2\text{O} + 3\text{AgCl} + \text{CO}_2 + \text{CO}$, a colourless pun-

gent liquid, easily converted by alcohol into trichloroacetic acid and its ethyl salt.

V. H. V.

Action of Ethyl Bromide on Ethyl Bromacetate. By L. ARONSTEIN (*Ber.*, **14**, 606—607).—The author considers that the formation of ethylene iodide and ethyl acetate by the action of ethyl iodide on ethyl iodacetate is probably due to the decomposition of ethyl iodide into ethylene and hydriodic acid, the latter reducing the ethyl iodacetate to ethyl acetate, whilst the former combines with the liberated iodine. In order to confirm this view, ethyl bromide was heated with ethyl bromacetate, and the principal products of the reactions were ethylene, hydrobromic acid, and bromoacetic acid.

The ethyl bromide is thus decomposed into ethylene and hydrobromic acid, and this latter acts on the ethyl bromacetate thus: $\text{HBr} + \text{CH}_2\text{Br.COOEt} = \text{EtBr} + \text{CH}_2\text{Br.COOH}$.

V. H. V.

Action of Methyl Iodide on Methyl Iodoacetate. By L. ARONSTEIN and J. M. A. KRAMPS (*Ber.*, **14**, 634—605).—The authors have shown that ethyl iodide and ethyl iodoacetate heated together form ethyl acetate and ethylene iodide (this *Journal*, *Abstr.*, 1880, 541), but the authors have found that a similar reaction between methyl iodide and methyl iodoacetate does not take place, carbon, iodine, methyl acetate, and various other decomposition products being produced.

V. H. V.

Etheric or Lampic Acid. By L. LEGLER (*Ber.*, **14**, 602—604).—Kingzett (this *Journal*, 1880, *Trans.*, 792) supposes that the oxidation of turpentine and ether is attended by the formation of a peroxidised product, which converts water into hydrogen peroxide. The author has re-examined this substance prepared from ether, and finds it to be a definite chemical substance and not a mixture of formic and acetic acids, aldehyde and acetal. A ready method of preparation consists in passing a mixture of ether vapour and air over red-hot platinum. Lampic acid, with the alkalis and alkaline earths, gives a mixture of methaldehyde, hydrogen peroxide, acetic and formic acids; with ammonia, hexmethylenamine; with lead protoxide and peroxide, detonating gas; and with alkaline permanganate, ordinary oxygen. This compound is fairly stable in dilute acidulated water; concentrated solutions are decomposed slowly with formation of paramethaldehyde; it crystallises in long needles, which are slightly volatile, and, under certain circumstances, decompose with explosive violence.

V. H. V.

Chromium Barium Oxalate. By F. W. CLARKE and E. A. KEBLER (*Ber.*, **14**, 36).—This salt, first obtained by Rees-Reece in dark-violet silky needles, containing 12 or 18 mols. H_2O , has been obtained by the authors in a green modification crystallising with 7 or 12 mols. H_2O . The compound $\text{C}_{12}\text{Cr}_2\text{Ba}_3\text{O}_{24} \cdot 12\text{H}_2\text{O}$, forms dark green silky needles of sp. gr. 2.372 at 27° . The salt with $7\text{H}_2\text{O}$ is paler and of sp. gr. 2.896 at 28° .

J. R.

Ethyl Chloromalonate. By M. CONRAD (*Ber.*, **14**, 617—620).—A continuation of the author's former researches (this Journal, Abstr., 1880, 627—629). Ethyl isobutylchloromalonate by saponification yields *isobutyltartronic acid*, which in its turn is converted by heat into carbonic and *hydroxyisobutylacetic acids*; the zinc salt of the latter crystallises in silky scales.

By decomposing barium ethyltartronate, the acid, $(\text{COOH})_2\text{C}_2\text{Et}_3\text{OH}$, is obtained in a crystalline form; it is decomposed by heat, and also by dilute hydrochloric acid into carbonic and α -*hydroxybutyric acids*.

The ethyl salt of formyltricarboxylic acid unites with chlorine to form a monochloro-derivative, $(\text{COOEt})_3\text{CCl}$, which boils at 210° . By an analogous reaction the ethyl salt of dibromacetylenetetracarboxylic acid was obtained.

As a result of the author's researches, it is found that the chloro-substitution derivatives of the ethereal salts of the alcoholic malonic acids are converted by acids and alkalis into alcoholic tartronic acids, which, by heating at 180° , are decomposed into carbonic anhydride and alcoholic hydroxyacetic acids. The ethereal salts of the alcoholic malonic acids, however, behave differently when a second negative radical is combined with the same carbon-atom as the chlorine.

Thus by the saponification of ethyl chloroformyltricarboxylate, $(\text{COOEt})_3\text{CCl}$, carbonic anhydride is always evolved, and it is not possible to obtain a tribasic hydroxy-acid, the product being a dibasic hydroxy-acid, or an unsaturated acid, accordingly as acids or alkalis are used for saponification.

V. H. V.

A Neutral Bromide from Diallylmalonic Acid. By E. HJELT (*Ber.*, **14**, 627—628).—By passing bromine into an aqueous or acetic acid solution of diallylmalonic acid, white glistening crystals (m. p. 130°) of a bromine compound separate out, insoluble in cold, but soluble in warm water, alcohol, and ether. The compound has a composition intermediate between $\text{C}_9\text{H}_{12}\text{O}_4\text{Br}_2$ and $\text{C}_9\text{H}_{10}\text{O}_4\text{Br}_2$; and is perfectly neutral. From its analogies with Bredt and Fittig's lactone, the author considers that the compound is a double lactone. By the action of hydrobromic acid on diallylmalonic acid, the author has obtained a neutral crystalline substance (m. p. 108°), probably a bromine free lactone.

V. H. V.

Preparation of Monobromo- and Dibromo-succinic Acids. By G. SCHACHERL (*Ber.*, **14**, 637).—These acids may be conveniently prepared by heating 1 mol. ethyl succinate with 2 mols. bromine in a sealed tube at 130 — 140° .

V. H. V.

Action of Ammonia on Ethyl Dibromosuccinate. By A. CLAUS and J. HELPENSTEIN (*Ber.*, **14**, 624—627).—The authors were unable to obtain ethyl dibromosuccinamate by the action of ammonia on ethyl dibromosuccinate, as the ammonia always removes the bromine-atom; in this respect, ethyl dibromosuccinate differs from its analogue ethyl chloromalonate. The authors found that the action of ammonia

on ethyl dibromosuccinate gave rise to ethyl diamidosuccinate and diamidosuccinamide.

Ethyl diamidosuccinate, $\text{COOEt} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}(\text{NH}_2) \cdot \text{COOEt}$, crystallises in needles or rhombic prisms (m. p. 122°), easily soluble in alcohol and ether, but quite insoluble in water.

Diamidosuccinamide, $\text{CONH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}(\text{NH}_2) \cdot \text{CONH}_2$, forms long delicate needles (m. p. 160°) insoluble in ether and water.

By the action of alkalis, both these compounds are easily converted into diamidosuccinic acid, which forms white needles (m. p. 151°), soluble in ether and alcohol. The alkali salts of this acid are easily soluble in water, and give white precipitates with silver and lead salts, and a bright green precipitate with copper salts. V. H. V.

Azelaic Acid. By F. GANTTER and C. HELL (*Ber.*, **14**, 560—566). —The authors have made a complete examination of azelaic acid (obtained by the oxidation of castor-oil) and its salts. The acid was separated from suberic acid by fractional precipitation of an ethereal solution of the calcium salts of the mixed acids.

Azelaic acid melts at 106° and re-solidifies into large crystalline leaflets, but if contaminated with 1 per cent. of suberic acid it solidifies in warty aggregates. The acid is less soluble in water, but more soluble in ether than suberic acid; it is not volatile in a current of steam; it distils (at a temperature above the range of the thermometer) unchanged, without formation of an anhydride. Strong nitric acid acts on the acid but very slowly, succinic acid being among the products of oxidation. On comparing the salts of azelaic with those of suberic acid (Abstracts, 1880, 872—875), it is found that those of the former are, on an average, about three times more soluble than those of the latter. Again, the suberic acid salts are more soluble in cold than in hot water, whilst of the azelaic salts some are more soluble in cold than in hot water, others more soluble in hot than in cold, others equally soluble at both temperatures. Further differences are observable in the water of crystallisation of the salts of these acids.

Metal.	Formula.	Form.	Solubility in 100 parts H_2O .	Remarks.
Potassium	$\text{K}_2\text{C}_9\text{H}_{14}\text{O}_4$	Delicate glistening crystals, deliquescent.		
Hydrogen potassium	$\text{KHC}_9\text{H}_{14}\text{O}_4$	White crystalline mass.		
Tetracid potassium } Tassium .. }	$\text{KHC}_9\text{H}_{14}\text{O}_4$ } $\text{H}_2\text{C}_9\text{H}_{13}\text{O}_4$ }			
Sodium	$\text{Na}_2\text{C}_9\text{H}_{14}\text{O}_4 \cdot \text{H}_2\text{O}$.	Glistening leaflets soluble in water, but not deliquescent.		
Hydrogen sodium	$\text{NaH} \cdot \text{C}_9\text{H}_{14}\text{O}_4$...	Spherical crystals.		
Ammonium ...	$(\text{NH}_4)_2\text{C}_9\text{H}_{14}\text{O}_4$..	Large glistening leaflets.	Is decomposed at 110° into the free acid and ammonia.

Metal.	Formula.	Form.	Solubility in 100 parts H ₂ O.	Remarks.
Hydrogen ammonium	NH ₄ C ₉ H ₁₅ O ₄ ...	Glistening leaflets.		
Barium	BaC ₉ H ₁₄ O ₄ .H ₂ O .	Crystalline crust	At 16·5° = 0·650 At 100° = 0·628	
Strontium	SrC ₉ H ₁₄ O ₄ .H ₂ O..	At 18° = 0·930 At 100° = 1·853	
Calcium	CaC ₉ H ₁₄ O ₄	White crystalline powder	At 17° = 0·186 At 100° = 0·193	
Magnesium ...	MgC ₉ H ₁₄ O ₄ .3H ₂ O	Large leafy glistening crystals.	At 18° = 3·62 At 100° = 4·73	
Aluminium	White voluminous precipitate.		
Ferric	Red-brown precipitate.		
Manganese ...	MnC ₉ H ₂₄ O ₄ .3H ₂ O	A white precipitate consisting of fine needles.	At 14° = 0·206 At 100° = 0·108	
Nickel	NiC ₉ H ₁₄ O ₄ .6H ₂ O	Well formed apple-green prisms.	At 16° = 0·683 At 100° = 0·563	
Cobalt	COH ₃ H ₁₄ O ₄ .6H ₂ O	Light red six-sided tables	At 13° = 0·693 At 100° = 0·224	The salts dried at 100° become blue-violet.
Zinc	ZnC ₉ H ₁₄ O ₄	White crystalline precipitate	At 12° = 0·027	
Cadmium	CdC ₉ H ₁₄ O ₄	White precipitate of small glistening needles.	At 18° = 0·065	
Copper	CuC ₉ H ₁₄ O ₄	Bluish-green voluminous precipitate.	At 23° = 0·01	
Lead	PbC ₉ H ₁₄ O ₄	Heavy pulverulent precipitate	At 24° = 0·006	
Mercurous	White crystalline precipitate.		
Mercuric	White finely pulverulent precipitate.		
Silver	Ag ₂ C ₉ H ₁₄ O ₄	White pulverulent voluminous precipitate.	At 14° = 0·015	
Free acid	At 12° = 0·108	

V. H. V.

β -Methylethenyltricarboxylic Acid. By A. BISCHOFF and M. GUTHZEIT (*Ber.*, **14**, 614—617).—The authors have more fully investigated propenyltricarboxylic acid (this vol., Abstr., 156) and have isolated the free acid, (COOH)₂CH.CHMe.COOH. The acid forms a white, glistening crystalline mass, easily soluble in ether, alcohol, and water; on heating, it melts at 142°, decomposing into carbonic and pyrotartaric acids,



Propenyltricarboxylic acid is intermediate between ethenyltricarboxylic acid (cf. *supra*) and acetylenetetra-carboxylic acids.

By the action of bromine, methylethenyltricarboxylic is converted into a monobromopyrotartaric acid, which differs from the known monobromomethylsuccinic acid. The former is obtained as glistening white prisms (m. p. 202—204°); the barium and silver salts are insoluble. A second product of the action of bromine on propenyltri-

carboxylic acid is probably identical with Michael and Norton's δ -bromocrotonic acid, $\text{CHMe} : \text{CBr}.\text{COOH}$. V. H. V.

Preparation of Potassium Hydrogen Saccharate. By T. BAYLEY (*Chem. News*, **43**, 110).—To a saturated solution of pure cane-sugar an equal bulk of strong nitric acid is added, and after the evolution of gas has ceased, the mixture is boiled. It is then, while hot, divided into equal parts, and one-half neutralised with a strong solution of potash. To this the other half is added, when, after a short time, an abundant precipitate of acid saccharate is obtained. This can be purified by passing the hot solution over animal charcoal, evaporating to a small bulk, and recrystallising. D. B.

Potassium Lactonate. By H. KILIANI (*Ber.*, **14**, 651—652).—The author, with Haushofer, has made a crystallographic examination of potassium lactonate from lactose. It forms clinorhombic crystals whose axial relations are $a : b : c = 1.7663 : 1 : 2.0033$; $\beta = 76.35$ of combination $0\text{P} \cdot \infty\text{P} \cdot \text{P} \cdot \bar{\text{P}} \infty \cdot \frac{3}{2}\bar{\text{P}}\infty$.

The plane of the optic axes is at right angles to the plane of symmetry. Potassium lactonate from milk-sugar forms similar crystals.

V. H. V.

Solubility of Carbon Bisulphide in Water. By W. T. PAGE (*Chem. News*, **42**, 195).—The author found that the solubility of carbon bisulphide in water diminishes with rise of temperature; but, so far as shown by the following determinations, this diminution does not occur at a rate equal to that at which the vapour tension of carbon bisulphide increases, as shown by the tables of Renault and Marx:—

Time of contact with water.	Average temperature nearly constant.	Solubility of CS_2 .
30 days.	12—13° C.	0.203 in 100 by weight.
Do.	Do.	0.198 "
55 days.	15—16°	0.191 "
7 "	25—27	0.168 "
27 "	30—33	0.146 "
Do.	Do.	0.113 "

D. B.

Dithioglycollic Acid. By P. CLAESSON (*Ber.*, **14**, 409—411).—Thioglycollic acid is easily oxidised to *dithioglycollic acid*,



by cupric and ferric salts, by iodine, and by exposure to the air. In order to prepare dithioglycollic acid, iodine is added to a solution of potassium thioglycollate until it begins to colour the liquid. The mixture is acidified with sulphuric acid and exhausted with ether free from alcohol. The acid can also be obtained by passing a current of air through a solution of potassium thioglycollate to which a small quantity of ferric chloride has been added.

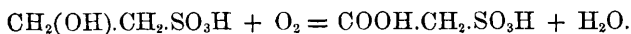
Dithioglycollic acid (m. p. 100°) precipitates lead and silver salts from their neutral solutions. Most of its salts are very soluble in water, and crystallise with difficulty. $\text{KS}_2\text{O}_4\text{C}_4\text{H}_5 + \text{H}_2\text{O}$ is deposited from

alcohol in needles, and the barium salt, $\text{BaS}_2\text{O}_4\text{C}_4\text{H}_4 + 4\text{H}_2\text{O}$, is precipitated from its aqueous solution on the addition of a small quantity of alcohol. The ethyl salt is a thick oily liquid, heavier than water (b. p. 280°). The amide (m. p. 155°) dissolves freely in hot alcohol.

Dithioglycollic acid is oxidised by potassium permanganate to thioacetic acid, and is reduced by zinc and dilute sulphuric acid to thio-glycollic acid.

W. C. W.

Isethionic Acid. By F. CARL (*Ber.*, **14**, 63—67).—By oxidation with chromic acid, isethionic acid is converted into sulphacetic acid, in accordance with the equation—

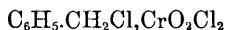


In a former paper (*Abstr.*, 1879, 28) the author showed that ammonium isethionate is transformed at 210° into the ammonium salt of di-isethionic acid. He now finds that barium isethionate behaves similarly. At 190 — 210° it is for the most part converted into di-isethionate.

J. R.

Chlorochromic Acid as an Oxidising Agent. By ÉTARD (*Ann. Chim. Phys.* [5], **22**, 218—286).—*Action on Toluene.*—The author dilutes the toluene with ten times its weight of carbon bisulphide in order to moderate the action which occurs when it is treated with the chromic dichloride. A chocolate coloured precipitate is formed which has the composition $\text{C}_6\text{H}_5\text{Me}.\text{2CrO}_2\text{Cl}_2$. In moist air or on addition of water it decomposes, with formation of benzaldehyde; and on treatment with ether, ethyl chloride and benzaldehyde are produced. By heating it at 240 — 250° it loses 2 mols. HCl , and yields $\text{C}_7\text{H}_6(\text{CrO}_2\text{Cl})_2$; this body does not decompose so easily in moist air as the previous one, but on treatment with water or ether it yields benzaldehyde. The author proposes to call the first compound benzylene-dichlorochromic acid, because of its resemblance to the corresponding disulphonic acid. For the second he proposes the name chlorobenzylene-dichromous acid, $\text{C}_6\text{H}_5.\text{CH}(\text{O}.\text{CrOCl})_2$.

Action of Benzyl Chloride.—A body of the composition



is formed, which on treatment with water yields benzaldehyde. On heating it loses HCl , and forms $\text{C}_6\text{H}_5.\text{CHCl}.\text{O}.\text{CrOCl}$. By acting on hot benzyl chloride with chromyl chloride, an oily fluorescent liquid is obtained (b. p. above 360°). The action of the acid, therefore, varies with the temperature.

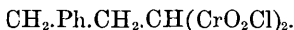
Action on Parabromotoluene.—By acting on a mixture of the isomeric bromotoluenes, the compound $\text{C}_6\text{H}_4\text{Br}.\text{CH}(\text{CrO}_2\text{Cl})_2$ is obtained. On treating this with water it gives bromobenzaldehyde, which on further oxidation yields parabromobenzoic acid (m. p. 251°). The chlorochromic acid separates the isomerides, choosing the one which is most readily attacked.

Action on Xylene.—A mixture of ortho- and meta-dimethylbenzene gives with chlorochromic acid the compound $\text{C}_6\text{H}_4\text{Me}_2.\text{2CrO}_2\text{Cl}_2$. On

treatment with water, metamethylbenzaldehyde, $C_6H_4Me.CO.H$, is formed (b. p. 198°). It oxidises spontaneously in the air, and is converted into metatoluic acid (m. p. 105°). On heating the compound $C_6H_4Me_2.2CrO_2Cl_2$, it loses $2HCl$ and forms $C_6H_4Me.CH(2CrO_2Cl)_2$.

Action on Ethylbenzene.—Chlorochromic acid gives the compound $CH_3Ph.CH[CrO(OH)Cl_2]_2$, which on treatment with water yields phenylacetaldehyde (b. p. $192-193^\circ$, m. p. -10°), and on further oxidation with chromic acid it gives benzoic acid. Canizzaro obtained the same compound by the dry distillation of a mixture of calcium formate and phenylacetate.

Action on Propylbenzene.—The propylbenzene employed (b. p. 167°) was diluted with carbon bisulphide. With chlorochromic acid, it yields *phenylpropylenedichlorochromic acid*, $C_6H_5(C_3H_7).2CrO_2Cl_2$. On heating, this gives *phenylpropylenedichromous chloride*,



On treatment with water it decomposes, with formation of hydrocinamic aldehyde.

Action on Diethylbenzene.—This compound treated with chlorochromic acid, yields *phenylethylethylidenedichlorochromic acid*, $C_{10}H_{14}.2CrO_2Cl_2$; and on decomposing this compound with water, the hitherto unknown ethylphenylacetaldehyde, $C_6H_4Et.CH_2.CO.H$, is produced.

Action on Cymene.—The cymene (b. p. $174-176^\circ$) was diluted with ten parts of carbon bisulphide. With chlorochromic acid, it yields a mixture of isomeric compounds of the formula $C_{10}H_{14}.2CrO_2Cl_2$. On heating at $200-210^\circ$ it loses $2HCl$ and forms $C_{10}H_{12}.2CrO_2Cl$. When decomposed by water, it yields an oily liquid, which forms with sodium sulphite two salts, differing in solubility. The less soluble one yields a body of the composition $C_{10}H_{12}O$, which the author proposes to call *isocumic aldehyde* (m. p. 80° , b. p. about 220°). On oxidation it forms the corresponding *isocumic acid* (m. p. 51°). Its silver salt is thrown down as a white curdy precipitate, but rapidly changes into crystalline scales. The more soluble salt yields on decomposition *terecumic aldehyde* (b. p. $219-220^\circ$). By oxidation in the air it forms an acid which melts at $128-129^\circ$, and on fusion with potash it yields paratoluic acid. Kopp found 229° for the boiling point of the natural aldehyde.

From the above experiments, the author draws the following conclusions regarding the action of chlorochromic acid on the aromatic hydrocarbons:—

1. Hydrocarbons of a given constitution can always be converted into the corresponding aldehydes.

2. Aromatic hydrocarbons which contain one or more methyl groups form additive products with chromyl chloride.

3. Two molecules of acid attach themselves to that methyl carbon atom which has the most hydrogen.

4. The dichlorochromic compounds are decomposed by water, with formation of an aldehyde.

The author has made a series of experiments in order to discover

what happens when the aromatic nucleus is attacked. In the preceding experiments only the methyl groups are acted on.

Action on Benzene.—Chlorochromic acid gives with benzene $C_6H_4(CrO_2Cl)_2$. On treatment with water, this yields quinone, which, however, rapidly decomposes, with formation of quinhydrone.

Action on Nitrobenzene.—This compound acted on with chlorochromic acid, yields $C_6H_3(NO_2)(CrO_2Cl)_2$, which is decomposed by water, with formation of nitroquinone, $C_6H_3(NO_2)O_2$. It melts at 232° , and sublimes in brilliant yellowish-brown scales. It has an acid reaction, and dissolves in alkaline solutions, being reprecipitated on addition of acids.

Action on Nitrotoluene.—By acting on nitrotoluene with chlorochromic acid, the compound $C_7H_5(NO_2)2CrO_2Cl$ is formed, and on treating this with water, it yields methylnitroquinone, $C_6H_2Me(NO_2)O_2$ (m. p. 237°), which is soluble in alkalis and in alcohol, and sublimes in glittering scales, resembling benzoic acid.

On acting on paradibromobenzene with chlorochromic acid, the author finds that the bromine is replaced by chlorine, but no quinone is formed. On treating bromobenzene in the same way, a white substance melting at about 88° is obtained, probably bromoquinone. Naphthalene and anthracene also yield quinones.

Action on Terebenthene.—By acting on terebenthene with chlorochromic acid, a body of the formula $C_{10}H_{16}.2CrO_2Cl$ is formed. Water decomposes it, with formation of an oil which boils at 190° , and which is probably terebic or dihydrocuminic aldehyde, $C_{10}H_{14}O$. This body is intermediate between cuminic aldehyde and camphor.

The author has shown that other terebic hydrocarbons yield chlorochromic compounds, which on treatment with water yield corresponding camphor-aldehydes.

Action on Hydrocarbons of the Fatty Series.—These hydrocarbons when treated with chlorochromic acid yield bodies with the general formula $X(CrO_2Cl)_2$, which form corresponding aldehydes when decomposed by water.

Action on Anethol.—When acted on with chlorochromic acid, anethol yields, after treatment with water, anisic aldehyde, $MeO.C_6H_4.CO.H$.

Action on Phenol.—Phenol unites with chlorochromic acid, forming a compound which with water gives $(C_6H_4.OH)_2O$.

Acetic acid and chlorochromic acid form a salt of the composition $Cr_2O_7.2[Cr_2(C_2H_3O_2)^5].8H_2O$.

The author's work shows that chlorochromic acid acts as follows:—

1. It forms organo-chromic compounds of the general formula $X(CrO_2Cl)_2$, in which X represents an aromatic hydrocarbon.

2. It converts methyl groups which are attached to an aromatic nucleus into aldehyde groups.

3. It attacks the aromatic nuclei, with formation of quinones.

J. I. W.

Action of Nitrogen Peroxide on Carbon Compounds. By A. R. LEEDS (*Ber.*, **14**, 482—485).—Toluene saturated with nitrogen peroxide was found after an interval of several months to have been converted into a mixture of oxalic, benzoic, and dihydroxybenzoic acids, orthonitrotoluene, and dinitro-*orcinol*. The dihydroxybenzoic acid is freely soluble in hot water, benzene, chloroform, and alcohol. It sublimes at 170° without melting. The silver salt and the free acid form anhydrous crystals. Ferric chloride does not produce any coloration. This acid therefore differs in its properties from the four known dihydroxybenzoic acids.

The dinitro-*orcinol* crystallises in golden needles (m. p. 110°). With baryta it yields a neutral salt, and it combines with paratoluidine to form the crystalline compound $C_7H_9N, C_7H_6(NO_2)_2O_2$. It is isomeric with the dinitro-*orcinol*, which Stenhouse and Groves (*this Journal*, **10**, 548) obtained by the action of dilute nitric acid on nitroso-*orcinol*.

Xylene treated with nitrogen peroxide yields orthonitroxylene, together with oxalic, paratoluic, and phthalic acids. Cymene yields α -nitrocymene, together with oxalic and paratoluic acids. Phenol is converted into picric acid, and anthracene into anthraquinone. W. C. W.

Decomposition of Dimethylaniline Methiodide and Ethiodide by Potash, and Action of Amyl Bromide on Dimethylaniline. By A. CLAUS and P. RAUTENBERG (*Ber.*, **14**, 620—623).—In order to explain the decomposition of the alcoholic halogen salts of the quinine bases by supposing an intermolecular change, like that of methylaniline into toluidine, the authors have endeavoured to convert dimethylaniline methiodide and ethiodide into the hydriodide of dimethyltoluidine by heating with potash, but without success.

Methylamylaniline.—By heating together at 150—160° in a sealed tube a mixture of 1 mol. amyl bromide with 2 mols. dimethylaniline, the authors have obtained methylamylaniline, one of the methyl groups in dimethylaniline being replaced by the amyl group, thus—



This base is a colourless liquid (b. p. 257°, sp. gr. 0.0906). It forms a crystalline platinochloride and a dark brown crystalline bismuthiodide $2(C_{12}H_{19}N, HI), 3BiI_3$.

When amyl bromide acts on dimethylaniline, the reaction is entirely different, one of the decomposition products being amylene.

V. H. V.

α - and β -Ethylc Dibenzoylethylhydroxamate and α - and β -Ethylbenzoylethylhydroxamic Acid. By O. GÜRKE (*Annalen*, **205**, 279—294).—Lossen has shown (*Annalen*, **186**, 4) that of the seven compounds obtained from hydroxylamine by replacement of the 3 atoms of hydrogen by benzoyl and anisyl, six are polymorphous. A more intimate examination of Eiseler's ethylc dibenzoylethylhydroxamate (*ibid.*, **175**, 327) shows that it is dimorphous.

α -Ethylc dibenzoylethylhydroxamate, NBz_2EtO . The product of the action of ethyl iodide on silver dibenzoylethylhydroxamate consists chiefly of

this modification. M. p. 58° . Sp. gr. at 18.4° , 1.2433. It darkens when heated above its melting point, decomposing rapidly at 185° , the temperature, even after removal of the flame, rising to 260° , and benzoic acid, benzonitril, and aldehyde being produced, $N(Ph.CO)_2.C_2H_5O = NPh + Ph.COOH + C_2H_4O$. Dibenzoylhydroxamic acid itself decomposes thus:— $N(PhCO)_2HO = N(CO)Ph + Ph.COOH$.

β -Ethyllic dibenzoylhydroxamate, NBz_2EtO , forms 2 or 3 per cent. of the product of the action of ethyl iodide on silver dibenzoylhydroxamate, crystallising out last. M. p. 63° ; more readily soluble than the α -modification in alcohol and ether, but insoluble in water and light petroleum. Sp. gr. 1.2395 at 18.4° . Hydrochloric acid produces the same products as in the case of the α -modification, viz., benzoic acid, ethyl benzoate, and hydroxylamine. On dry distillation, the same products are formed as from the α -modification, the β -modification beginning to decompose only at about 225° .

An excess of concentrated potash produces β -ethylbenzoylhydroxamic acid. The two modifications are quite distinct crystallographically. All attempts to transform one modification into the other failed.

α -Ethylbenzoylhydroxamic acid, $NBzHEtO$, obtained by the action of potash on α -ethyl dibenzoylhydroxamate. M. p. 53.5° . Sp. gr. 1.2072—1.2099.

On heating, decomposition commences at about 180° , and is very irregular, the chief products being benzonitrile, ethyl benzoate, alcohol, water, and nitrogen; in smaller quantities benzamide, benzoic acid, nitric oxide, and carbonic anhydride are formed.

β -ethylbenzoylhydroxamic acid, $NBzHEtO$, obtained as above. M. p. 67.5° to 68° . Sp. gr. 1.1839—1.1867. It yields the same products as the α -modification, both on heating and by the action of hydrochloric acid.

Lossen remarks on the preceding paper that the designation of the modifications of ethylic dibenzoylhydroxamate and ethyl benzhydroxamic acid as *physical isomerides* agrees tolerably well with ordinary usage, inasmuch as the chemical differences between these bodies are unimportant, and cannot well be attributed to a different linking together of the atoms within the molecule. He pointed out in a former paper (*Annalen*, 186, 52) that the different modifications of one and the same hydroxylamine derivative may perhaps be regarded as polymerically related to one another, in the same manner as aldehyde and paraldehyde.

F. L. T.

Phthalyl-hydroxylamine: Conversion of Phthalic into Salicylic Acid. By L. COHN (*Annalen*, 205, 295—314).—*Phthalyl-hydroxylamine* is prepared by dissolving hydroxylamine hydrochloride in a small quantity of water, and acting on it alternately with small portions of sodium carbonate and phthalic chloride free from phosphorus compounds, the mixture being kept always alkaline, and these additions continued so long as free hydroxylamine could be detected. The fluid is gradually transformed into a red coloured magma, consisting almost exclusively of phthalyl-hydroxylamine; the red colour is due to the formation of its sodium salt by the excess of sodium carbonate. Phthalyl-hydroxylamine is obtained as

a white precipitate on decomposing the solution of the sodium salt by hydrochloric acid. The yield is not very large, two experiments giving 21.6 and 55.5 per cent. respectively of the theoretical yield. Phthalyl-hydroxylamine, as shown by Rotermond, behaves just like an acid, expelling carbonic anhydride from its salts, and combining with bases to form salts. Somewhat soluble in water, readily in alcohol; insoluble in ether, benzene, and carbon bisulphide, dissolving in the caustic alkalis with a red colour. Melts at 230° (uncorr.), undergoing decomposition with evolution of nitrogen. Its composition is $N(C_8H_4O_2)HO$. All its salts are brightly coloured; those more intimately examined are:—Potassium (red), sodium (red), silver (dark red), lead (yellow red), barium (bright red). The following gave precipitates with the potassium salt:—Cupric sulphate (green, only in concentrated solutions); manganese sulphate (bright brown), chrome alum (egg-yellow), mercurous nitrate (brownish), mercuric chloride (orange-yellow), cobalt nitrate and nickel sulphate gave no precipitate.

Ethyl-phthalyl-hydroxylamine, $C_{10}H_9NO_3$, was prepared by acting on the silver salt of phthalyl-hydroxylamine in presence of ether, with ethyl iodide, and leaving the liquid for three or four days in the dark. The ethereal solution yields colourless crystals of ethyl-phthalyl-hydroxylamine (m. p. $103-104^{\circ}$ uncorr.).

By heating hydroxamic acid in which a mono-carbon acid residue is introduced, the carboxyl group of the acid employed can be replaced by amidogen (*Annalen*, **175**, 315). Phthalyl-hydroxylamine should yield the corresponding phenylenediamine, but in spite of numerous experiments neither this nor other bases containing carbon could be found. Benzoic acid sublimes, and nitrogen is evolved, an odour of hydrocyanic acid being produced each time on heating.

Action of Potash on Phthalyl-hydroxylamine.—Carboxyl is replaced by amidogen, not only by heating but also by boiling the salts of the alkalis with water (*Annalen*, **175**, 257). By the action of alcoholic potash (1 mol.), and boiling for about an hour, and then evaporating and adding hydrochloric acid, orthamidobenzoic acid was obtained, and may be converted into salicylic acid by the action of nitrous acid in presence of sulphuric acid.

On warming 10 grams phthalyl-hydroxylamine for a short time on the water-bath, with an amount of alcoholic potash equivalent to 2 mols., a clear solution was obtained, depositing large quantities of a potassium salt on cooling, of the composition $C_8H_6NO_4K$. The author regards this salt as that of an acid standing in the same relation to hydroxylamine as the unknown phthalamic acid stands to ammonia. He proposes to call it hydroxylphthalamic acid. The solution of the potassium salt gives white precipitates with plumbic and mercurous nitrates; precipitates occur only in concentrated solutions with silver nitrate, barium chloride, strontium chloride, calcium chloride, and chrome alum; no precipitate with magnesium sulphate, cobalt nitrate, nickel sulphate, or mercuric chloride. The free acid has as yet been obtained in solution only, by decomposing the lead salt with hydrogen sulphide. On standing, it deposits crystals of phthalyl-hydroxyl-

amine. By heating phthalyl-hydroxylamine with concentrated potash solution, ammonia, hydroxylamine, and phthalic acid are formed.

No particular results were obtained by heating ethyl phthalyl-hydroxylamine with potash. Ethyl-phthalyl-hydroxylamine distils with but very slight decomposition at about 270° , giving a distinct odour of aldehyde.

The author concludes by pointing to a possible analogy between hydroxylamine and V. Meyer's nitrolic acids (*Annalen*, **175**, 88), the group NOH being attached to a bivalent residue in both.

F. L. T.

Condensation-products of Aromatic Bases. By O. FISCHER (*Annalen*, **206**, 85—159).—The author has already communicated (*Ber.*, **9**, 1753; **10**, 952; and abstracts in this Journal, **34**, 51; **36**, 53; **38**, 39, 40, 636, 661, and 662) most of the results described in this paper.

Aromatic Acids and Tertiary Bases.—By heating 1 part benzoic acid and 1 part dimethylaniline with phosphoric anhydride, in a sealed tube, at 180 — 200° for eight hours, benzoildimethylaniline (*Ber.*, **9**, 958) is formed; it is a weak base, and melts at 38 — 39° . By dissolving in strong nitric acid, it is converted into a dinitro-derivative, soluble in alcohol, but insoluble in water (m. p. 142°). The hydrol formed by reducing this base could not be crystallised; it distilled with decomposition, the distillate at first light yellow, became blue on standing, and then green. Benzoildimethylorthotoluidine is obtained in a similar manner to the dimethylaniline derivative; it distils between 350 — 360° , and is soluble in light petroleum, from which it crystallises in tufts of colourless, glistening spear-heads (m. p. 67°).

From phthalic anhydride, dimethylaniline and zinc chloride, the author obtained a green substance, which is a mixture of two bodies, one colourless, dimethylanilinephthalein, the other green. If the temperature rises too high, another base, $C_{17}H_{22}N_2$, is formed, m. p. 90° , yielding quinone on oxidation. The colourless base crystallises in thick shining prisms (m. p. 190 — 191°), soluble in benzene, toluene, sparingly in ether or alcohol, and insoluble in water. It distils in small quantities without decomposition. By heating gently with concentrated sulphuric acid, it dissolves to a red-violet solution, which on raising the temperature turns brown-red to dirty brown; water precipitates a dark-green flocky substance, soluble in ether. Its salts are mostly soluble in water. The dihydrochloride, $C_{24}H_{24}N_2O_2 \cdot 2HCl$, is a colourless, hygroscopic precipitate, which on heating for some time at 100° , loses 1 mol. of hydrochloric acid, and is converted into the monohydrochloride, $C_{24}H_{24}N_2O_2 \cdot HCl$, a colourless crystalline powder, slightly soluble in water; at 160° it turns green. The picrate, $C_{24}H_{24}N_2O_2 + 2C_6H_3N_3O_7$, yellow needles, very sparingly soluble in water. The platinochloride, $2(C_{24}H_{24}N_2O_2 \cdot HCl) \cdot PtCl_4$, from the monohydrochloride, is a yellow crystalline precipitate, whilst that from the dihydrochloride, $C_{24}H_{24}N_2O_2 \cdot 2HCl \cdot PtCl_4 \cdot OH_2$, is reddish-yellow. The methiodide, $C_{24}H_{24}N_2O_2 \cdot CH_3I$, prepared by heating the phthalein with excess of methyl iodide at 100 — 110° , forms groups of colourless needles, soluble

in hot water, in alcohol, and wood spirit; sparingly in cold water. At 185° it melts and decomposes, giving off methyl iodide.

Hexnitrodimethylanilinephthalein.—The preparation of this body from impure materials has been already described (*Ber.*, **10**, 954); it forms yellow, hexagonal plates, soluble in hot glacial acetic acid; it decomposes at 230° . Bromine acts violently on the phthalein, and gives uncrystallisable products. By fusion with potash, phthalic and benzoic acids are formed, and a body smelling like carbylamine. By reduction it gives dimethylanilinephthalin (*loc. cit.* 952) which crystallises from hot alcohol in brilliant leaflets, easily soluble in ether and benzene. It dissolves both in dilute alkalis and in acids; it turns yellow when kept, melts at about 200° , and decomposes when heated above this temperature, forming an oil, which gives a blue-green coloration with chloranil. The phthalin warmed with strong sulphuric acid dissolves with a blue-violet colour, which turns reddish by further heating; from this solution alkalis precipitate a base, soluble in ether. *Tetramethyldiamidotriphenylmethane* is produced when a mixture of the phthalin and barium hydrate is carefully heated. When phthalic chloride is used in the preparation of this phthalein (*Ber.*, **12**, 1692), and the product treated with light petroleum, the phthalein remains undissolved; the solution on standing deposits tetramethyldiamidotriphenylmethane, which is a bye-product, whilst the mother-liquor retains the green colouring matter, mixed with small quantities of these two bases. To separate them, the mixed monohydrochlorides are dissolved in alcohol, and on adding a small quantity of water to this solution, the hydrochloride of the green base is precipitated. Its constitution is $C_{24}H_{24}N_2O_2 \cdot HCl$; it forms yellowish-green needles, only slightly soluble in water. It gives a zincchloride crystallising in brassy-yellow needles, soluble in water. The solutions dye silk green. The leuco-base, $C_{24}H_{24}N_2O$, is easily made by digesting the crude product from the action of phthalic chloride on dimethylaniline with hydrochloric acid and zinc-dust, filtering, treating the filtrate with excess of soda, shaking out with benzene, evaporating down the dried benzene solution, and adding excess of dry ether; the leuco-base then separates out. It forms hard, bright small prisms, melting at 235 — 236° ; soluble only in hot benzene, toluene, and chloroform. The leuco-base is easily changed into the green base by oxidation; even by exposure to the air. Nitric acid converts both these bases into phthalic acid.

Products from the Alcohols and Tertiary Aromatic Bases (compare this Journal, **36**, 53).—Benzyl alcohol and dimethylaniline, digested with zinc chloride at 150° , give an oily base, distilling between 330 — 340° , probably identical with Michler and Grandmann's dimethylamidodiphenylmethane (this Journal, **34**, 299). Benzhydrol and dimethylaniline in a similar way yield dimethylamidotriphenylmethane—which the author has also prepared from benzophenone and dimethylaniline (*Ber.*, **12**, 1690)—a weak base; soluble in ether, light petroleum, and benzene; melting at 132° . Its salts are not very soluble in water. The platinumchloride, $(C_{24}H_{24}N_2 \cdot HCl)_2 \cdot PtCl_4$, forms yellow crystals, which turn reddish in the air; the methiodide crystallises in colourless, glittering leaflets, melting at 184 — 185° , and identical with the one from the

author and L. Roser's methylated amidotriphenylmethane (this Journal, **38**, 661).

Products from the Aldehydes and Dimethylaniline.—Those from methylal (this Journal, **38**, 40); from chloral (*ibid.*, **36**, 53); from benzaldehyde (*ibid.*, **33**, 52; **38**, 40); from cuminol and dimethylaniline (*Ber.*, **12**, 1688; this Journal, **38**, 640); and from benzaldehyde and dimethyltoluidines (this Journal, **38**, 626), have been described; to these may be added the description of the following salts of tetramethyldiamidotriphenylmethane: the platinochloride, $C_{23}H_{26}N_2 \cdot 2HCl \cdot PtCl_4$, a light yellow substance; the aurochloride, $C_{23}H_{26}N_2 \cdot 2HCl \cdot 2AuCl_3$, light yellow crystals, soluble in alcohol, on warming the solution it oxidises and turns green; the picrate, $C_{23}H_{26}N_2 \cdot [C_6H_4(NO_2)_3(OH)]_2$, crystallises from alcohol in yellowish-green needles, insoluble in ether and water. There is a long account of "malachite-green," in which the author describes six methods of preparation and several of its salts, already noticed in the papers above referred to. The product, $C_{21}H_{24}N_2O$, from furfural and dimethylaniline (this Journal, 1878; *Abstr.*, 51; *Ber.*, **11**, 951) gives: a platinochloride, $C_{21}H_{24}N_2O \cdot 2HCl \cdot PtCl_4$, a light yellow precipitate, which turns red in the air; an aurochloride, soluble in alcohol, from which solution it separates out as a crystalline powder; and a picrate, $C_{21}H_{24}N_2O \cdot 2(C_6H_4(OH)(NO_2)_3)$, crystallising in greenish-yellow microscopic needles, insoluble in cold alcohol. The compound $C_{21}H_{24}N_2O \cdot Br_2$ (?) is formed on treating it with the required quantity of bromine; by further action of this reagent hydrobromic acid is evolved, with the production of the hydrobromide of a brominated base, which is precipitated by alkalis from an aqueous solution in dark green flocks. It is soluble in concentrated hydrochloric acid to a red solution, and in sulphuric acid to a red-violet solution; these solutions, when diluted, are green, like the alcoholic solutions. With dimethylaniline, salicylaldehyde and (1:4) hydroxybenzaldehyde yield dye-stuffs allied to "malachite-green," but containing the OH groups intact; the solutions of the product from the latter are red by transmission, and green by reflected light.

Condensation-products of Primary Aromatic Bases. Aldehydes and Primary Bases.—Diamidotriphenylmethane (this Journal, **38**, 661).—The best method of preparing this body is as follows:—To a mixture of aniline hydrochloride (13 parts) and zinc chloride (13 parts), warmed on a water-bath, benzaldehyde (16 parts) is added; the mass is kept liquid by pouring in water, and the reaction completed by heating at 110 – 120° for eight hours. After separating the benzaldehyde and aniline the base is dissolved in dilute sulphuric acid, and reprecipitated by diluting this solution with water; the colourless flocks which fall out crystallise on standing. The diazo-compound gives triphenylmethane when boiled with alcohol, and with water yields dihydroxytriphenylmethane. The author sums up as follows:—

1. With alcohols (benzyl alcohol, benzhydrol), aromatic acids (benzoic acid), and bases, the reaction takes place with elimination of water, and the product formed is a combination of 1 mol. of the alcohol or acid with 1 mol. of the base.

2. With aldehydes and base, water is formed, and the product contains 2 mols. of the base with 1 mol. of the aldehyde.

3. Anhydrides (benzoic anhydride and phthalic anhydride) behave like aldehydes.

4. With halogen derivatives of the paraffins (CCl_3H , CCl_4 , C_2Cl_6) and benzene hydrocarbons (PhCH_2Cl , PhCHCl_2 , PhCCl_3) hydrochloric acid is set free, and each chlorine atom removed is displaced by a residue of the base, but the products contain at the most three phenyl residues combined with one carbon atom, for one carbon atom, it seems, cannot unite with more than three benzene groups.

5. With acid chlorides (COCl_2 , PhCOCl) the condensation can take place in two ways, either (1) with elimination of hydrochloric acid and the formation of a ketone; or (2) with the expulsion of water in an analogous way to the aldehydes.

It is probable that the relative position of the amido-groups to the combining carbon is always the same, viz., 1 : 4. D. A. L.

Thymoquinonechlorimide. By M. ANDRESEN (*J. pr. Chem.* [2], **23**, 167—196). — R. Hirsch (*Ber.*, **11**, 1980) has shown that the substance obtained by the action of paramidophenol hydrochloride on bleaching powder, and described as dichlorazophenol, could not be an azo-compound, but must be considered as chloroquinoneimide, $\text{C}_6\text{H}_3\text{Cl}(\text{ONH})$. The author has examined the corresponding thymoquinonechlorimide. The thymol used for its preparation had a melting point of 51° against 44° , as usually stated, but was perfectly pure. Sodium thymolate, by treatment with potassium nitrite and sulphuric acid, was converted first into nitrosothymol, and then by reduction into paramidothymol. This, treated with calcium hypochlorite solution, furnished the imide in the form of a yellow oil, of penetrating quinone-like odour, remaining liquid at -21° . It volatilises when distilled with water, but cannot be distilled *per se*, as it decomposes with explosive violence between 160° and 170° . Its composition corresponds with the formula $\text{C}_{10}\text{H}_{12}\text{NClO}$. The corresponding bromine derivative could not be obtained, the action of calcium hypobromite on paramidothymol giving rise to thymoquinone.

When thymoquinonechlorimide is heated with fuming hydrochloric acid, chlorine is evolved, and a crystalline yellow magma is obtained: ether extracts a yellow oil from this, and leaves *monochloramidothymol hydrochloride*, which, after crystallisation from alcohol, is obtained in the form of long colourless needles, subliming without decomposition when carefully heated. The portion soluble in ether consists of *dichlorothymoquinone* and *monochlorothymoquinone*, the former crystallising in large rhombic plates (m. p. 99°), turning brown on exposure to daylight, the latter, which could not be obtained in a pure condition, being a mobile yellow oil.

With sodium carbonate monochloramidothymol hydrochloride gives a precipitate of the base, soluble with green coloration in an excess of the precipitant, insoluble in water, crystallising from alcohol and ether in large glistening needles or prisms (m. p. 100.5°).

Monochlorodiazothymol hydrochloride, obtained by the action of nitrous acid on the amido-compound, crystallises from a mixture of ether and alcohol in long, colourless, often fan-like needles, exploding on the application of heat.

Thymoquinonechlorimide, heated with hydrobromic acid, yields *monobromamidothymol hydrochloride*, insoluble in ether, crystallising from water in colourless needles, and *dibromothymoquinone*, identical with that described by Carstanjen, and probably *monobromothymoquinone*.

If sulphurous acid is passed into water containing thymoquinonechlorimide in suspension, this dissolves with formation of *thymoquinol* (m. p. 139°).

By reduction with tin and hydrochloric acid, the imide also yields thymoquinol, together with paramidothymol. O. H.

Absorption Spectra of Chrysoïdine and Related Azo Colouring-matters. By J. LANDAUER (*Ber.*, **14**, 391—394).—Alcoholic solutions of chrysoïdine and of other amidoazo-compounds belonging to the same family exhibit an absorption of the blue rays of the spectrum. The addition of hydrochloric acid changes the colour of the solutions from yellow to red, and causes an absorption in the green portion of the spectrum. W. C. W.

Benzolone and Benzostilbene. By H. M. RAU (*Ber.*, **14**, 443—445).—When hydrobenzamide is fused with potash, lophine is formed. The two non-nitrogenous compounds, benzolone and benzostilbene, which Rochleder (*Annalen*, **41**, 93) obtained by this reaction, could not be detected. W. C. W.

Action of Glacial Acetic Acid on Phenylthiocarbimide. By A. CLAUS and M. VÖLTZKOW (*Ber.*, **14**, 445—446).—Phenylthiocarbimide is decomposed by glacial acetic acid at 160°, with formation of sulphuretted hydrogen, carbonic anhydride, carbonyl sulphide, and acetanilide. Attempts to prepare the anilide of chloracetic acid by the action of aniline on an ethereal salt of chloracetic acid have not been successful. W. C. W.

Compounds of Monobasic and Dibasic Acids with Phenols. By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], **23**, 147—156).—Resorcinol, heated with glacial acetic acid in presence of zinc chloride, readily combines with the acid, and yields *dioxyacetophenone*, $C_6H_5\cdot\overset{\text{Ac}}{\underset{\text{O}_2}{C}}$ (m. p. 142°), distilling between 303° and 305°, and crystallising in rhombic laminæ or needles. It is soluble without decomposition in concentrated sulphuric acid, and is not altered by boiling alkalis or acids. Heated with acetic anhydride, it furnishes *diacetylresorcinol* (m. p. 72°), identical with that described by Malin, and obtained by him from the action of acetic chloride on resorcinol.

An alcoholic solution of dioxyacetophenone, mixed with alcoholic soda, at once yields needles of a sodium salt, of varying composition, which readily decomposes on drying. Oxidised with chromic mixture, oxyacetophenone furnishes acetic acid, and with nitric acid, *mononitrodioxyacetophenone*, crystallising from 50 per cent. alcohol in beautiful long pale-yellow needles (m. p. 142°). In presence of zinc

chloride, resorcinol also combines with butyric acid and formic acid. These products have not yet been examined.

Succinic acid, heated at 190—195° with resorcinol and sulphuric acid, readily yields *succinylfluoresceïn*, first discovered, but not further studied by Baeyer (*Ber.*, 1871, 662). It has the composition $C_{16}H_{12}O_5 + 3H_2O$, crystallises from dilute hydrochloric acid in brown crystals, and readily loses a part of its water of crystallisation over sulphuric acid. With bromine or hydrobromic acid its hydrochloric acid solution yields a red amorphous precipitate of *tetrabromsuccinylfluoresceïn*, $C_{16}H_8Br_4O_5$, which may be obtained in small red needles by precipitating its solution in alkalis by hydrochloric acid. It is a dibasic acid, its acid potassium salt, $C_{16}H_7Br_4O_5K$, forming brown-red shining rhombic needles. Similar sodium and ammonium compounds have been obtained, all readily soluble in hot water. The calcium and barium salts are insoluble in water, and form red crystalline precipitates. O. H.

Action of Aromatic Hydroxy-acids on Phenols. By A. MICHAEL (*Ber.*, 14, 656—658).—It is probable that the numerous plant substances which are decomposed by alkalis into aromatic hydroxy-acids and phenols are polyhydric hydroxybenzophenones or simple derivatives of them. But only one such substance has been obtained by a synthetical process, viz., paradihydroxybenzophenone (*Abstracts*, 1878, 887).

On heating together a mixture of phenol and salicylic acid with zinc chloride, a golden-red mass is obtained, which may be purified by repeatedly dissolving in alkali and reprecipitating by carbonic acid. The compound salicylphenol thus obtained has the composition $C_{13}H_{10}O_3$, formed thus: $C_6H_4(OH).COOH + C_6H_5.OH = CO(C_6H_4.OH)_2 + H_2O$. It crystallises from alcohol in glistening golden needles (m. p. 143—144°), insoluble in cold water, easily soluble in hot benzene and alcohol. It combines with zinc chloride to form a compound crystallising in needles. With acetic anhydride it forms a diacetyl derivative, crystallising in white needles or prisms (m. p. 87—88°), easily soluble in hot alcohol, sparingly soluble in hot water. On reducing an alkaline solution of salicylphenol with sodium amalgam, it is converted into the corresponding dihydroxybenzhydrol, $CH(C_6H_4.OH)_2$, a white amorphous body (m. p. 160—165°), insoluble in cold water, easily soluble in hot alcohol.

Resorcinol and salicylic acid, when heated together even without the addition of a dehydrating agent, form a trihydric hydroxybenzophenone, $C_6H_4(OH).COOH + C_6H_4(OH)_2 = C_6H_4(OH).CO.C_6H_3(OH)_2 + H_2O$. This compound forms pale golden crystals (m. p. 133—134°), easily soluble in hot water, alcohol, and benzene; it dissolves also in warm dilute solutions of the alkaline carbonates, from which it may be reprecipitated by carbonic acid. The author believes that by the action of hydroxysalicylic acid on quinol, he has synthetically prepared euxanthone. V. H. V.

Cresol Derivatives. By A. W. HOFMANN and W. v. MILLER (*Ber.*, 14, 567—574).—As only five of the many theoretically possible nitro-

derivatives of cresol have at present been obtained, the authors have made a more exact study of these compounds. Commercial cresol, prepared from crude orthotoluidine, was dissolved in acetic acid and acted on with nitric acid (sp. gr. 1.4), diluted with acetic acid. On adding water, an oil is precipitated, which is partly volatile in a current of steam, leaving a resinous residue, which was not further examined. The portion which passes over with the steam can be separated into one dinitro- and three mononitro-compounds.

Dinitrocresol can be separated from the more volatile mononitro-cresols by fractional distillation in a current of steam. It melts at 83° , and is identical with the dinitrocresol obtained by Beilstein and Kreisler, Armstrong and Field, and others.

Mononitrocresol (m. p. 69.5°), which distils over first, forms long golden prisms, soluble in alcohol and ether, insoluble in water; its potassium compound crystallises in rhombic tables, and its silver compound in red needles.

The nitrocresol can be best converted into its methyl ether by heating in a sealed tube to $115-120^{\circ}$ a mixture of potassium nitrocresol with methyl iodide. On reduction, the methyl ether gives amidocresolmethyl ether, $C_6H_3Me(NH_2).OMe$, a liquid (b. p. 223°) insoluble in water. In order to determine the constitution of this nitrocresol, the product obtained by nitrating pure *orthocresol* was examined, and found to be identical with that obtained from the commercial cresol. When the amidocresol obtained from this nitrocresol was distilled with sodium formate, a crystalline methenyl compound was obtained (m. p. $38-39^{\circ}$; b. p. 200°). As the experiments of Hübner and Ladenburg have shown that only those amidophenols, in which the hydroxyl and amido-groups are in contiguous positions form a methenyl compound, it follows that this nitrocresol has the constitution $[Me : OH : NO_2 = 1 : 2 : 3]$.

Liquid mononitrocresol (b. p. $226-230^{\circ}$) forms metallic derivatives closely resembling those of the solid nitrocresol, but amidocresol methyl ether is solid (m. p. $52-53^{\circ}$). This nitrocresol is also derived from *orthocresol*, and it is probable that the hydroxyl- and nitro-groupings are in the *para*-position. A methenyl compound was obtained from the corresponding amidocresol, but the authors consider it probable that its formation was due to an impurity of *orthonitroparacresol* (*vide infra*).

Mononitrocresol (m. p. 33°), identical with that obtained by Armstrong and Thorpe by the nitration of *paracresol*. The corresponding amidocresol forms a methenyl compound (m. p. 45°), thus showing that this nitrocresol has the constitution $[Me : NO_2 : OH = 1 : 3 : 4]$. The amidocresol methyl-ether is a crystalline compound (m. p. $36-38^{\circ}$). In the nitration of *paracresol* the authors observed the formation of acetic and propionic acids, which they conjecture is due to the splitting up of the benzene nucleus by the nitric acid.

Erlenmeyer, in the oxidation of the hydroxybenzoic acids, has observed a similar decomposition.

V. H. V.

Synthesis of Thymol. By E. PATERNÒ and F. CANZONERI

(*Gazzetta*, **11**, 124--137).—As natural thymol and that prepared artificially from cymene both yield the same cymene and the same thymoquinone, it seems probable that they are both derived from parapropylmethylbenzene, and that the isomerism depends on the difference in position of the OH-group. In order to solve this question, the author has endeavoured to prepare from cymene a new phenol, in which the OH-group occupies a different position from what it does in carvacrol, either through bromocymenesulphonic acid or through the liquid nitrocymene.

Bromocymenesulphonic Acid, $C_6H_2MePrBr.SO_3H + 3H_2O$.—As it was found that the action of sulphuric acid on bromocymene gave rise to a mixture of sulphonic acids very difficult to separate, recourse was had to sulphonic monochloride, which acts readily on bromocymene with evolution of hydrochloric acid. On adding water to the product, *bromocymenesulphonic chloride*, $C_6H_2MePrBr.SO_2Cl$, is precipitated as a heavy oil, which crystallises on standing, whilst the bromocymenesulphonic acid remains in solution, and is converted into the barium salt by neutralisation with barium carbonate. *Barium bromocymenesulphonate*, $(C_6H_2MePrBr.SO_3)_2Ba + 5H_2O$, crystallises in plates or prisms. The *lead salt*, containing $4H_2O$, forms iridescent scales, and when decomposed by hydrogen sulphide, yields a solution of the acid, which may be obtained in large prismatic tables, by slow evaporation: when anhydrous, the acid melts at $130-132^\circ$. The *potassium* and *ammonium salts* are both crystalline, and the former is very soluble both in water and in alcohol. Bromocymenesulphonic chloride, as already stated, is obtained in the preparation of the acid, and is also produced by the action of phosphorus pentachloride on the potassium salt of the sulphonic acid; it crystallises from ether in large transparent prisms (m. p. $80-81^\circ$). The *amide*, $C_6H_2MePrBr.SO_2NH_2$, prepared by the action of alcoholic ammonia at 110° on the chloride, crystallises in white silky needles (m. p. 191°), almost insoluble in water, but easily soluble in alcohol or ether. An attempt was made to displace the bromine in this amide by hydrogen by the action of reducing agents, so as to obtain the sulphonic acid isomeric with that formed by the action of sulphuric acid on cymene; the displacement of the SO_3H -group in this by OH should then yield a phenol isomeric with carvacrol, and possibly identical with thymol. The results, however, were not satisfactory; for although a crystalline compound (m. p. 112°) was obtained free from bromine, differing from the ordinary cymenesulphonamide, great difficulties were experienced in the reduction.

The authors also give detailed results of two experiments on the action of sulphuric acid on bromocymene, from which they infer that in this reaction all three of the possible bromocymenesulphonic acids are formed.

The second attempt at the synthesis of thymol was made through the liquid nitrocymene. This was reduced by iron turnings and acetic acid, and yielded a cymidine, boiling at $248-250^\circ$: the yield, however, is but small, and no better results were obtained with tin and hydrochloric acid. This base was converted into the sulphate by adding sulphuric acid to the ethereal solution, and then suspended in water and treated with nitrous acid. As the sulphate of the diazo-

compound could not be isolated, the solution was largely diluted and boiled, when a brown oily substance separated. This, on being submitted to distillation in a current of steam, yielded a yellow oil, having all the characters of a phenol, whilst a considerable quantity of a resinous substance remained in the retort. The dry phenol boiled at 228—234°, but as the quantity was too small for complete purification and careful study, it was converted into the nitroso-compound, which, after crystallisation from benzene, melted at 152—153°; that is at the same temperature as the derivative from camphothymol, the nitroso-compound from natural thymol melting at 155—156°. As these melting points are so near, whilst there is a considerable difference between the corresponding nitro-derivatives (79° and 137°), it was thought advisable to convert the nitroso- into the nitro-compound by potassium ferricyanide, but the result was unsatisfactory, as the small quantity of oily product could not be obtained in a crystalline state. The author suspects, however, that the phenol is really camphothymol.

C. E. G.

Bromonitro- and Chloronitro-phenetoils. By E. J. HALLOCK (*Ber.*, 14, 36—38).—A bromonitrophenetoil is readily obtained by first acting on phenetol with bromine, and then treating the bromophenetol thereby formed with nitric acid: it crystallises in pale-yellow needles (m. p. 47°), and is regarded as parabromo-orthonitrophenetoil. Another body, of the same composition, obtained by the action of bromine on paranitrophenetoil, melts at 55°, and in accordance with the mode of formation, is to be regarded as orthobromo-paranitrophenetoil.

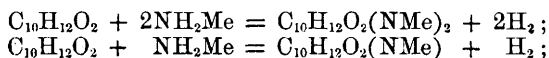
Similarly, two chloronitrophenetoils have been obtained. Pure phenetol, treated with potassium chlorate and hydrochloric acid, yields a chlorophenetol, which is converted by nitric acid into parachloro-orthonitrophenetoil (m. p. 61°). The isomeric compound, orthochloro-paranitrophenetoil, obtained by treating paranitrophenetoil with potassium chlorate, melts at 78°.

All these bodies are reduced by tin and hydrochloric acid, yielding amido-compounds.

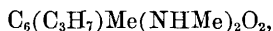
Paranitrophenetoil is obtained, although in very small proportion, by the direct action of fuming nitric acid on phenetoil. It melts at 58°, and by reduction yields amidophenetol, boiling at 253°. J. R.

A Derivative of Quinol. By G. MAGATTI (*Ber.*, 14, 70).—Mononitrodimethylquinol is readily converted into the corresponding amido-compound, which is a crystalline basic substance melting at 74—75°, and boiling with partial decomposition at 270°. Its hydrochloride crystallises from alcohol in slender needles. J. R.

Action of Amines on Quinones (II). By T. ZINCKE (*Ber.*, 14, 92—98).—Thymoquinone in alcoholic solution reacts with methylamine in the following ways:—



the two reactions taking place simultaneously. The product of the first reaction, *dimethamido-* or *dimethylido-thymoquinone*,



crystallises from hot alcohol in reddish-violet needles (m. p. 203°). It reacts with benzoic chloride to form a *dibenzoyl derivative* and with acetic chloride in apparently the same manner. When boiled with sulphuric acid or alcoholic potash, it yields methylamine and *dihydroxy-thymoquinone*, $\text{C}_{10}\text{H}_{15}(\text{OH})_2\text{O}_2$. The last product (which is identical with Ladenburg's) crystallises in fine red needles or prisms (m. p. 213°), and forms crystallisable barium and lead salts. The crystalline diacetyl-compound, $\text{C}_{10}\text{H}_{10}(\text{O}\ddot{\text{A}}\text{c})_2\text{O}_2$, melts at 81° ; the dibenzoyl-compound at 163° .

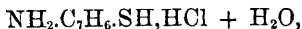
The product of the second of the above reactions, *methylamido-* or *methylido-thymoquinone*, $\text{C}_6\text{H}(\text{C}_3\text{H}_7)\text{Me}(\text{NHMe})\text{O}_2$, crystallises in nearly black laminae, which melt at 74° . It reacts with benzoic and acetic chlorides in the same manner as the dimethyl-compound. In alcoholic solution, it is easily decomposed by hydrochloric and sulphuric acids, yielding methylamine and *hydroxythymoquinone*, $\text{C}_{10}\text{H}_{11}(\text{OH})\text{O}_2$ (m. p. 174 — 175°). J. R.

Benzhydryl Acetate. By C. VINCENT (*Bull. Soc. Chim.* [2], 35, 304).—By the action of glacial acetic acid on benzhydrol, Linnemann obtained benzhydryl acetate, which he described as a colourless oily liquid (b. p. 301 — 302° at 731 mm.), not solidifying at -15° . Friedel and Balsohn obtained the same product by treating monobromodiphenylmethane with potassium acetate in presence of glacial acetic acid. The author has repeated these experiments, and has obtained benzhydryl acetate, which crystallised readily after some hours' standing, especially if the excess of acetic acid were removed by washing with water. Large crystals deposited by slow evaporation from an acetic acid solution, fused at 41.5° and boiled without decomposition at 300° , giving a colourless distillate, which solidified in the receiver. The acetate is extremely soluble in acetic acid, and readily forms oily supersaturated solutions, a fact which will account for its having been described as a liquid by previous observers. C. H. B.

Amidotoluenesulphydrates. By C. HESSE (*Ber.*, 14, 488—496).—Paranitrotolueneorthosulphonic acid forms a chloride (m. p. 44°) which yields amidotoluene-sulphydrate (m. p. 42°) on reduction with tin and hydrochloric acid. This compound is soluble in alcohol, ether, alkalis, and acids; with mercuric chloride, it produces a silky, and with basic lead acetate a yellow flocculent precipitate. The hydrochloride crystallises in prisms or hexagonal plates; it is converted into the disulphide by boiling with ferric chloride. Amidotoluenesulphydrate forms a crystalline acetic compound, $\text{HS}\cdot\text{C}_7\text{H}_6\cdot\text{NH}\cdot\ddot{\text{A}}\text{c}$, melting at 195° .

When orthonitrotoluene is treated with fuming sulphuric acid at 150 — 160° , a sulphonic acid is produced which yields a chloride crystallising in plates (m. p. 36°). On reduction with tin and hydrochloric

ric acid, it is converted into the sulphhydrate, a colourless oil soluble in alcohol, ether, acids, and alkalis. The hydrochloride,



crystallises in hexagonal plates. It forms precipitates with lead acetate and mercuric chloride.

The nitrotoluenesulphonic acid, prepared by the action of sulphuric acid at 120° on orthonitrotoluene, forms a liquid chloride, which yields a thick oily sulphhydrate on reduction. The hydrochloride crystallises in needles. On treatment with acetic anhydride, orthamidotolueneparasulphhydrate forms a crystalline compound which melts at 240° .

The two amidomercaptans from orthonitrotoluene can also be prepared from the two amidosulphonic acids which are obtained by the action of strong nitric acid on orthotoluidine.

The sulphhydrate from orthonitrotolueneparasulphonic acid is identical with orthamidotolueneparasulphhydrate.

From paramidotoluenemetasulphonic chloride an oily sulphhydrate is obtained, which oxidises slowly in the air, is precipitated by lead and mercuric salts, and forms a crystalline hydrochloride, $\text{NH}_2\cdot\text{C}_7\text{H}_6\cdot\text{SH}, \text{HCl}$. When boiled with acid anhydrides or chlorides it yields anhydro-bases.

Methenylamidotoluenemercaptan, $\text{C}_7\text{H}_6 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{CH}$, melts at 15° and

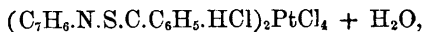
boils at 255° . It is soluble in alcohol and ether, and forms unstable salts. The platinochloride crystallises in needles.

Ethenylamidotoluenemercaptan, $\text{C}_7\text{H}_6 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}_2\cdot\text{CH}_3$, resembles the

preceding compound.

Benzenylamidotoluenemercaptan, $\text{C}_7\text{H}_6 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}\cdot\text{C}_6\text{H}_5$, crystallises in

needles (m. p. 125°). The hydrochloride, crystallising in plates, is decomposed by water. The platinochloride,



forms needle-shaped crystals.

W. C. W.

Cuminoïn. By O. WIDMAN (*Ber.*, **14**, 609—610).—The author has studied the preparation and properties of cuminoïn investigated lately by Bösler (*Ber.*, **14**, 323). It forms delicate white needles (m. p. 101° , Bösler, 98°), and can be converted by acetic anhydride into an acetyl derivative, $\text{C}_9\text{H}_{11}\cdot\text{CH}(\text{AcO})\cdot\text{C}_9\text{H}_{11}$. This forms glistening transparent four-sided tables or prisms (m. p. 95°), which exhibit a great tendency to superfusion. The author has also established that cuminoïn cannot be oxidised to cumil by nitric acid, but only by dry chlorine (Bösler) and (preferably) by chromic acid.

V. H. V.

Organic Fluorine Compounds. By E. PATERNO (*Gazzetta*, **11**, 90—92).—Although Schmitt and Gehren's fluobenzoic acid (m. p.

182°), prepared by the action of hydrofluoric acid on diamidobenzoic acid, is generally believed to be the meta-derivative, the authors, on preparing the para-compound in a similar manner from paranitrobenzoic acid, obtained a fluobenzoic acid of m. p. 182°, and agreeing perfectly in its chemical properties with Schmitt and Gehren's acid. On converting pure metamidobenzoic acid into the corresponding fluobenzoic acid, a product was obtained melting at 123°, and quite different from the acid which melts at 182°. It is very difficult to explain this discrepancy, for although the action of nitric acid on benzoic acid gives rise to all three of the nitrobenzoic acids, Griess has shown that the proportion of the para-derivative produced is but very small as compared with the others. It would seem, however, that the fluobenzoic acid (m. p. 182°) obtained by Schmitt and Gehren, is not the meta-derivative as hitherto supposed, but the para-compound derived from paramidobenzoic acid. Metafluobenzoic acid melts at 123° and yields crystalline *barium* and *calcium* salts. The *methyl* salt is a liquid of b. p. 192—194°. The fluorine derivatives would appear to melt at lower temperatures than the corresponding chlorine derivatives. The parachloro- and parafluorobenzoic compounds melting at 236° and 182° respectively, whilst the corresponding meta-compounds melt at 153° and 123°. The author is engaged in investigating the ortho-fluoroderivative, which, however, cannot be prepared so easily as the other two.

An attempt to prepare fluoracetic acid by the action of silver fluoride on chloracetic acid was unsuccessful, the products being silver chloracetate and hydrofluoric acid.

C. E. G.

Barium and Calcium Cinnamates. By O. REBUFFAT (*Gazzetta*, **11**, 165—166).—It is usually stated that barium cinnamate crystallises with 1 mol. H_2O , and the calcium salt with $3H_2O$, or, according to Selmi, with $1\frac{1}{2}H_2O$. The author, who has most carefully examined these salts, finds that barium cinnamate crystallises either in micaceous scales or in striated prisms, which appear to be built up of the scales: the results of 16 analyses show that both forms contain 2 mols. H_2O , and have the formula $(C_9H_7O_2)_2Ba + 2H_2O$. Calcium cinnamate, prepared from either form of the barium salt, has the formula $(C_9H_7O_2)_2Ca + 3H_2O$.

C. E. G.

Orthhydrazincinnamic Acid. By E. FISCHER (*Ber.*, **14**, 478—482).—When sodium nitrite is added to a solution of amidocinnamic acid in hydrochloric acid, a mixture of orthodiazocinnamic nitrate and chloride is deposited as a yellow crystalline powder. The crude product dissolves in an aqueous solution of sodium sulphite, forming a dark red liquid which is acidified with acetic acid and decolorised by zinc-dust. The mixture is filtered, neutralised, saturated with common salt, and finally acidified with glacial acetic acid, which precipitates the sulphonate in yellow crystals soluble in pure water. By boiling the aqueous solution with hydrochloric acid until the yellow colour disappears, *hydrazincinnamic anhydride* or *amidocarbostyryl* is formed. On the addition of an alkali, it is precipitated as a colourless oil which solidifies to a crystalline mass (m. p. 127°). The anhydride,

$\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{N}(\text{NH}_2) \end{smallmatrix} > \text{CO}$, is soluble in water, and dissolves in concentrated hydrochloric acid, forming a hydrochloride crystallising in prisms. It does not reduce alkaline silver or copper solutions. The hydrochloric acid solution is decomposed by sodium nitrite, with the formation of carbostyryl.

A mixture of diazo- and nitroso-compounds is produced by the action of sodium nitrite and dilute sulphuric acid on ethylamidocinnamic acid. The nitrosamine, $\text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_3\text{O}_2 \cdot \text{NEt} \cdot \text{NO}$, is separated from the diazocinnamic acid by treatment with cold alcohol, from which solution it is deposited in pale-yellow plates (m. p. 149°). On reduction with zinc and acetic acid, it is partially converted into a hydrazone
W. C. W.

Hydroxytoluic and Hydroxyphthalic Acids. By O. JACOBSEN (*Ber.*, **14**, 38—43).—Orthoxylenesulphonamide, dissolved in potash, is converted by oxidation with potassium permanganate into two isomeric sulphamic acids melting at 217° and 243° , both of which yield pure orthotoluic acid when heated with hydrochloric acid. These sulphamic acids, when fused with potash, are converted into hydroxytoluic acids, that which melts at 217° yielding an hydroxy-acid identical with Tiemann and Schotten's *metahomo-parahydroxybenzoic acid* (m. p. 179°), whilst that which melts at 243° yields *parahomo-metahydroxybenzoic acid* (m. p. 172°). By further oxidation with potassium permanganate, in presence of potash, the sulphamic acids are both converted into sulphamidophthalic acid, which by fusion with potash yields *hydroxy-orthophthalic acid* (m. p. 177 — 180°), identical with Baeyer's acid.

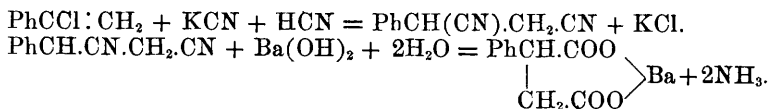
The relation of the three hydroxy-acids thus obtained to orthoxylenol, of which they may be regarded as oxidation-products, is shown by the following formulæ:—

		1.	2.	4.
Orthoxylenol,	C_6H_3	OH	CH_3	CH_3
Metahomoparahydroxybenzoic acid,	C_6H_3	OH	CH_3	COOH
Parahomometahydroxybenzoic acid,	C_6H_3	OH	COOH	CH_3
Hydroxyorthophthalic acid,	C_6H_3	OH	COOH	COOH

J. R.

Hydroxymesitylenic Acid from Xylenol. By O. JACOBSEN (*Ber.*, **14**, 43).—Liquid metaxylenol, treated with sodium and carbonic anhydride (Kolbe's reaction), is converted into orthhydroxymesitylenic acid, the yield of which is very large. The product being easily freed from impurities by crystallising its barium salt, crude liquid xyleneol may be used as the starting-point. The process is recommended as by far the best way of preparing hydroxymesitylenic acid in large quantity.
J. R.

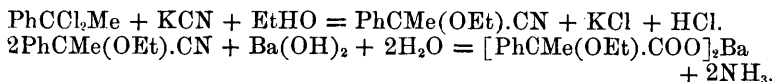
Phenylsuccinic Acid. By L. RÜGHEIMER (*Ber.*, **14**, 428—432).—An attempt to prepare the nitril of atropic acid by the action of potassium cyanide on an alcoholic solution of chlorostyrene at 200 — 220° , yielded a product which, when boiled with bartya-water, formed barium phenylsuccinate:—



Phenylsuccinic acid can be prepared synthetically by acting on a solution of sodium ethylacetoacetate in absolute alcohol with ethylic phenylbromacetate, $\text{PhCHBr}\cdot\text{COOEt}$; ethyl phenylacetosuccinate is produced, which, on saponification, yields phenylsuccinic acid (m. p. $159\cdot5$ — 162°). The acid is freely soluble in acetone, alcohol, and hot water. The lead and silver salts are sparingly soluble, but the calcium and barium salts dissolve readily in water.

The author considers it probable that the phenylfumaric acid of von Richter and Barisch (*J. pr. Chem.*, **20**, 186) is identical with phenylsuccinic acid. W. C. W.

Ethylatrolactic Acid. By L. RÜGHEIMER (*Ber.*, **14** 446—449).—*Ethylatrolactic acid*, prepared by saponifying the product of the action of ethyl bromhydratropate on sodium ethylate, is identical with the acid obtained from dichlorethylbenzene (*Ber.*, **13**, 2041, this volume, 171), by the following reactions:—



This synthesis supports the view that the formula for tropic acid is $\text{PhCH}(\text{CH}_2\cdot\text{OH})\cdot\text{COOH}$. The author believes that in Spiegel's synthesis (*Ber.*, **14**, 235) of tropic acid, by acting on acetophenone with nascent hydrocyanic acid, the nitrile of atrolactic acid is first formed, which is then converted into atropic acid by treatment with strong hydrochloric acid. W. C. W.

Formation of Aromatic Ketonic Acids. By O. DOEBNER (*Ber.*, **14**, 647—651).—As the author has already shown that a benzoyl group is easily introduced into the aromatic nucleus of phenols and anilines (1873, Abstr., 321; 1879, Abstr., 319; 1880, Abstr., 804), it seemed desirable to ascertain whether the same reaction occurs with other benzene derivatives, of which benzoic acid was taken as a typical aromatic acid.

Benzoylbenzoic acid, $\text{PhCO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is prepared by heating together benzoic chloride and benzoic anhydride with zinc chloride, the acid being extracted from the crude products of the reaction by hot water. It forms colourless leaflets (m. p. 160°), soluble in hot water, alcohol, ether, benzene, &c., and identical with the metabenzoylbenzoic acid obtained by Ador (this Journal, 1880, Abstr., 470). The author alludes to the fact that the benzoyl grouping enters into phenol and aniline in the *para*-position, but into benzoic acid in the *meta*-position. V. H. V.

Chemical Examination of Persea Lingue and its Tannin. By PEDRO N. ARATA (*Anales de la Sociedad científica Argentina*, **10**, 193—209).—The Lingue or *Persea Lingue* (*Laurus caustica*) is a tree

widely diffused in the Republic of Chili, between the Provinces of Aconcagua and Chiloé; and is also found in the territory between Limay and Neuquen, in the Argentine Republic. It grows to a height of 25 to 30 feet, and its stem is 2 feet in circumference. Its bark occurs in commerce in channelled pieces, 10 to 15 cm. broad, 5 to 9 mm. thick, and having a peculiar aromatic odour. Sp. gr. = 0.896. Its outer surface is very rugged and full of irregular cracks; it has a dark orange-colour, lighter round the cracks, and variegated with zones of white spots. The inner surface is smooth, but marked with longitudinal lines, which scarcely project above it; colour like that of the outer surface.

Proximate analysis gave:—

Water	2.526
Constituents soluble in ether: <i>Resins, essential oil,</i> and small quantities of <i>tannin</i>	17.714
Constituent soluble in alcohol: <i>Tannin</i>	24.630
Constituents soluble in water: <i>Proteids, gum,</i> <i>sugar, &c.</i>	14.551
Constituents soluble in dilute hydrochloric acid: <i>Calcium oxalate, &c.</i>	2.629
Woody fibre and loss	37.950
	<hr/>
	100.000

The ash was found to contain:—

Silica and carbon.	CO ₂ .	P ₂ O ₅ .	SO ₃ .	CaO.	MgO.	K ₂ O and Na ₂ O.
3.54	21.96	9.40	6.65	31.47	10.80	13.02

·Cl, Fe₂O₃ and loss.

3.16 = 100

The tannin of Lingue bark may be prepared by treating an aqueous decoction of the bark, after cooling and filtering, with basic lead acetate, to separate gummy matters, precipitating the filtrate with normal lead acetate, washing the precipitate with warm water out of contact with the air, removing the lead by hydrogen sulphide, and evaporating the filtrate out of contact with the air. Another mode of preparation is to precipitate the aqueous decoction, previously freed from mucilaginous matters, with sulphuric or hydrochloric acid, wash the precipitate to remove free acid, and dry it over sulphuric acid.

Lingue tannin, C₁₇H₁₇O₉, is a reddish-white powder, which becomes deep red on prolonged exposure to the air. Sp. gr. 1.352 at 15°. It is soluble in alcohol, acetic ether, acetone, and methyl alcohol, slightly soluble in water, insoluble in ether, chloroform, carbon bisulphide, and light petroleum. Its solutions give a green coloration with ferric chloride, and white or red precipitates with various metallic salts. By dry distillation, it yields water and catechol. By oxidation with nitric acid, it is converted into oxalic and picric acids. By prolonged heating with concentrated aqueous potash, it yields phloroglucol, together with a small quantity of an acid which appears to be protocatechuic acid.

The characters above described show that the tannin of *Persea Lingue* is analogous to that of *Quebracho colorado* (so-called *Quebrachogum*, this Journal, **34**, 986) and to those of catechu, gambir, kino, &c. H. W.

Schizomycetic Fermentation of Quinic Acid. By O. LOEW (*Ber.*, **14**, 453—452).—A solution of quinic acid, containing small quantities of potassium phosphate, magnesium sulphate, and peptone or ammonium sulphate, decomposes in presence of *schizomycetes*. If the fermentation takes place in an open vessel, protocatechuic acid is formed, but if air is excluded during the process, the quinic acid splits up into propionic, acetic, and formic acids. W. C. W.

Cymenesulphonic Acids. By P. SPICA (*Ber.*, **14**, 652—655).—On heating a mixture of cymene and sulphonic monochloride, and neutralising with barium carbonate, the barium salts of two cymenesulphonic acids are obtained, which may be separated by fractional crystallisation. The acids, $C_6H_3MePr^a.SO_3H$, have the constitution $Me : Pr^a : SO_3H = [1 : 4 : 3]$ and $[1 : 4 : 2]$ respectively. The $[1 : 4 : 3]$ acid crystallises in deliquescent prisms (m. p. 86°), and is converted by ammonia into a sulphonamide crystallising in needles (m. p. 73·5°). The barium salt, $(C_{10}H_{13}SO_3)_2Ba + H_2O$, crystallises in small tables, the lead salt, $(C_{10}H_3SO_3)_2Pb_3 + H_2O$, in opaque scales, the sodium salts, $C_{10}H_{13}SO_3Na + 3H_2O$ and H_2O , in large glistening scales.

The $[1 : 4 : 2]$ acid and its lead salt have all the properties of the so-called "normal" cymenesulphonic acid; it melts at 50—51 (Fittica above 270°). The barium salt described by Paternò, the author, and Claus (this vol., 174), is not a single substance but a mixture.

V. H. V.

Ethereal Salts of Phenyl and some of their Derivatives. By C. SCHIAPARELLI (*Gazzetta*, **11**, 65—82).—The author was in hopes of obtaining hydroxysulphobenzide, $PhSO_2.C_6H_4.OH$, by the action of phenylsulphonic chloride, $PhSO_2Cl$, on phenol in presence of zinc. The reaction takes place readily, with evolution of hydrochloric acid and formation of an oil, which may remain a considerable time without becoming crystalline, but solidifies almost immediately on adding a drop or two of potash solution. After being purified by crystallisation from alcohol, it forms colourless plates of silky aspect (m. p. 35°), moderately soluble in alcohol and ether, but insoluble in water; under the ordinary pressure, it distils with decomposition, evolving sulphurous anhydride, and yielding a liquid which has not as yet been examined. It has the composition $C_{12}H_{10}SO_3$, but as benzoic chloride has no action on it, it evidently does not contain an OH group, and is, therefore, not hydroxysulphobenzide. Alcoholic potash easily decomposes it, with formation of phenol and potassium phenylsulphonate, showing that the new compound is phenylic phenylsulphonate. The action of the zinc in this case is different from that observed by Zincke, as it merely serves to facilitate the evolution of hydrochloric acid without exerting any influence on the nature of the reaction, $Ph.SO_2Cl + Ph.OH = Ph.SO_2.OPh + HCl$. As the reaction takes place with the greatest facility at a comparatively low temperature (50—80°), and the product is nearly theoretical in quantity, it seemed

likely that zinc powder might be advantageously employed in the preparation of other ethereal salts of phenyl. This was found to be the case, the benzoate, acetate, and phosphate of phenyl being obtained with the greatest ease by this process. In the same way, the author prepared the *phenylsulphonate* of *paranitrophenyl*, and the *benzoates* of *para-* and *ortho-nitrophenyl*; the phenylsulphonate forms hard lustrous crystals (m. p. 82°) with striated faces, insoluble in water, but soluble in hot alcohol. Benzoate of paranitrophenyl crystallises in small colourless needles (m. p. 142°), insoluble in water, and but sparingly soluble in boiling alcohol: the orthonitrophenyl compound forms magnificent monoclinic prisms (m. p. 55°), moderately soluble in boiling alcohol.

By the action of a mixture of nitric acid (sp. gr. 1.5) and sulphuric acid on phenylic phenylsulphonate, a mixture of nitro-derivatives is obtained, from which a trinitro-derivative may be isolated by taking advantage of its comparative insolubility in boiling alcohol; it is a colourless crystalline powder (m. p. $115-116^{\circ}$), very soluble in benzene. The more soluble portion of the product, when decomposed by boiling with alcoholic potash, yields paranitrophenol and phenylsulphonic acid, so that it is a mononitro-derivative of phenylic phenylsulphonate, of the formula $\text{Ph} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. This compound alone is formed to the exclusion of the trinitro-derivative, when phenylic phenylsulphonate is acted on with nitric acid of sp. gr. 1.35 and sulphuric acid. The action of alcoholic potash on the trinitro-derivative did not give satisfactory results.

The reaction with phenyl benzoate is similar, a mononitro- or trinitro-derivative being produced according to the strength of the nitric acid employed.

Action of Phenylsulphonic Chloride on Phenylic Phenylsulphonate.—It seemed probable that if 2 mols. of the chloride were employed for each molecule of the phenylic salt, the reaction might take place in the following way:—



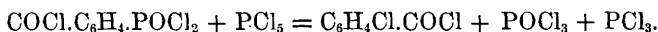
and that this product, when treated with potash, might split up, yielding potassium phenylsulphonate and hydroxysulphobenzide, $\text{PhSO}_2\text{C}_6\text{H}_4\text{O} \cdot \text{SO}_2\text{Ph} + \text{KHO} = \text{PhSO}_3\text{K} + \text{PhSO}_2\text{C}_6\text{H}_4\text{OH}$. With these proportions in presence of zinc powder the reaction takes place with great energy, but the products are phenylic phenylsulphonate and zinc phenylsulphonate. When, however, zinc chloride is substituted for zinc powder, the reaction takes place much more slowly, requiring four to five days for its completion, and the products are zinc phenylsulphonate, and a substance crystallising in fine prisms (m. p. 123°), easily soluble in hot alcohol. The results of the analyses of this substance agree with the formula $\text{PhSO}_2\text{C}_6\text{H}_4\text{O} \cdot \text{SO}_2\text{Ph}$, and it seems probable that by acting on it with potash, hydroxysulphobenzene may be obtained. The author is continuing the investigation.

C. E. G.

Benzophosphinic Acid. By A. MICHAELIS and C. PANEK (*Ber.*, 14, 405—408).—When a slightly alkaline solution of paratolylphos-

phinic acid, $\text{C}_6\text{H}_4\text{Me}.\text{PO}(\text{OH})_2$, is heated with potassium permanganate for several days at 50° , it is completely oxidised to *benzophosphinic acid*, $\text{COOH}.\text{C}_6\text{H}_4.\text{PO}(\text{OH})_2$. After removing the precipitated manganese dioxide, the filtrate is acidified with acetic acid and evaporated to dryness. The residue is treated with alcohol to dissolve out the potassium acetate, and the monopotassium benzophosphinate is dissolved in strong hydrochloric acid. On evaporating this solution at 50° , the free acid is deposited in glistening transparent plates, which dissolve freely in water, but are less soluble in alcohol. The acid melts above 300° , and at a somewhat higher temperature decomposes into benzoic and metaphosphoric acids and free carbon. It is not attacked by water and bromine at 130° . This acid is tribasic; the neutral silver salt is almost insoluble in water. *Monopotassium benzophosphinate*, $\text{COOK}.\text{C}_6\text{H}_4.\text{PO}(\text{OH})_2 + \text{H}_2\text{O}$, crystallises in needles, which dissolve in water, but are insoluble in alcohol: from the aqueous solution dilute hydrochloric acid precipitates the sparingly soluble acid salt $\text{COOK}.\text{C}_6\text{H}_4.\text{PO}(\text{OH})_2 + \text{COOH}.\text{C}_6\text{H}_4.\text{PO}(\text{OH})_2$. *Sodium benzophosphinate* has not been obtained in the crystalline state. Barium chloride and ferric chloride yield precipitates with the free acid.

Benzophosphinic chloride, $\text{COCl}.\text{C}_6\text{H}_4.\text{POCl}_2$, melts at 83° , and boils at 315° . It is decomposed by hot water, forming the free acid; by ammonia, forming the amide; and by alcohol, yielding a mixture of the neutral and acid ethereal salts. Benzophosphinic acid is decomposed by phosphorus penta-chloride at 200° , forming monochlorobenzoic chloride—



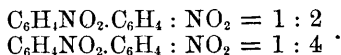
On treatment with water, monochlorobenzoic chloride yields paramonochlorobenzoic acid (m. p. 252°).

Methyl benzophosphinate, $\text{COOMe}.\text{C}_6\text{H}_4.\text{PO}(\text{OMe})_2$, is an uncrystallisable liquid, prepared by the action of methyl iodide on silver benzophosphinate.
W. C. W.

Diphenylene and δ -Diamidodiphenyl. By G. SCHULTZ and H. STRASSER (*Ber.*, **14**, 612—614).—By the action of concentrated nitric acid on diphenyl, two isomeric dinitrodiphenyls are formed, one of which (m. p. 233°) has been shown to be diparadinitrodiphenyl, whilst the other (isodinitrodiphenyl), m. p. 93.5° , is known to contain one nitrogen group in the para-position. The author has established, 1st, that the second nitro-group is in the ortho-position; 2nd, that the two nitro-groups are in different benzene nuclei; 3rd, that diamidodiphenyl from isodinitrodiphenyl is identical with δ -diamidodiphenyl from hydrazobenzene.

1st. Diphenyl in acetic acid solution when treated with nitric acid gives a paramononitrodiphenyl (m. p. 113°) and an isomeride (m. p. 37°). From this latter, a bromodiphenyl (b. p. 296 — 298°) is obtained, which is converted into orthobromobenzoic acid by oxidation; this shows that the nitrodiphenyl is an ortho-compound. But the nitrodiphenyl is easily converted into isodinitrodiphenyl, which is thus paranitro-orthonitrodiphenyl.

2nd. The parabromodiphenyl from isoamidodiphenyl by oxidation with chromic acid is converted into parabromobenzoic acid, which shows that the isodinitrodiphenyl has the nitro-groups in two different benzene nuclei, and is thus the orthopara-compound.



3rd. By heating hydrazobenzene with mineral acids, a diamidodiphenyl is formed, which is known as δ -diamidodiphenyl. From its method of preparation, the amido-groups must be in different benzene nuclei, and the authors establish its identity with diphenylene obtained by reduction from the isodinitrodiphenyl. The authors have also converted the two nitroamidodiphenylenes into the corresponding nitrohydroxydiphenyls. The diparahydroxydiphenyl forms needles (m. p. 170°), whilst the orthopara-compound melts at 138° . Latschinoff's parahydroxydiphenyl melts at 67° C. V. H. V.

Reactions of Benzidine. By A. CLAUS and E. RISLER (*Ber.*, **14**, 82—87).—When chlorine-water is added in small quantity to a solution of benzidine hydrochloride, the liquid assumes a fine blue colour, which on further addition of chlorine water passes into green; and ultimately, when the chlorine is in excess, a thick flocculent red precipitate is thrown down. This red body, after drying, forms a beautiful red satiny powder, soluble in hot alcohol, ether, and many other liquids, but not crystallisable. It explodes when heated, leaving charcoal. Its formula appears to be $\text{C}_{12}\text{H}_7\text{Cl}_3\text{N}_2\text{O}$, or that of benzidine in which three atoms of hydrogen are replaced by chlorine and two by oxygen. By reduction, it yields colourless compounds, which are now being investigated. Bromine acts on benzidine in a similar manner. The action of the halogens on benzidine is entirely different in presence of a large excess of hydrochloric or hydrobromic acid. Thus, bromine added to a solution of 1 part of benzidine and 25 parts of hydrobromic acid forms *tetrabromobenzidine*, a non-basic body subliming in delicate colourless needles (m. p. 284 — 286°). J. R.

Mononaphthylamines from Naphthols. By V. MERZ and W. WEITH (*Chem. News*, **42**, 302).—When α - or β -naphthol is heated at 270 — 280° with ammonium acetate and glacial acetic acid, or preferably a mixture of ammonium chloride and sodium acetate, only a mere trace of dinaphthylamine is formed, but in some cases more than 90 per cent. of the theoretical yield of α - or β -naphthylacetamine is obtained. $\text{NH}_4\text{AcO}_2 + \text{C}_{10}\text{H}_7\text{HO} = \text{NHAc}.\text{C}_{10}\text{H}_7 + 2\text{H}_2\text{O}$. When the acetyl compounds are heated with milk of lime under pressure, the primary amines are set free.

The two mononaphthylamines are also easily obtained in large quantity by heating the naphthols at 260° with ammoniacal calcium chloride made from the porous salt. The compound of calcium chloride with aniline, like that with ammonia, readily enters into chemical reactions. C. H. B.

Derivatives of β -Naphthylamine. By C. COSINER (*Ber.*, **14**, 58—63).—*Formo- β -naphthalide*, obtained by digesting β -naphthyl-

amine with ethyl formate in alcoholic solution, is a white crystalline body (m. p. 120°). Treatment with hot alkalis or dilute hydrochloric acid resolves it into its components.

Benzoyl- β -naphthalide is formed by the action of benzoic chloride on melted β -naphthylamine. The crystals melt at 141 — 143° . It is decomposed by hot alkalis.

Bromaceto- β -naphthalide is formed on mixing β -acetophthalide (m. p. 132° , obtained by digesting β -naphthylamine with excess of glacial acetic acid) with the required quantity of bromine, both dissolved in acetic acid. It melts at 134 — 135° . On boiling it with strong solution of potash, the acetyl-group is eliminated. The *bromo- β -naphthylamine* thereby formed crystallises in white needles (m. p. 63°). It is a perfectly neutral body, and does not combine with acids.

β -Naphthylacetophthalide, $C_{10}H_7.HN.CH_2.CO.NH.C_{10}H_7$, obtained by heating a mixture of 1 mol. of chloroacetic acid and 3 mols. of β -naphthylamine, crystallises in pale-yellow laminae (m. p. 170°).

β -Naphthylurethane, formed by the action of ethyl chlorocarbonate on β -naphthylamine in ethereal solution, crystallises in white flexible needles (m. p. 73°). It is resolved by hot potash solution or ammonia at 180° into carbonic anhydride, alcohol, and naphthylamine.

Mono- β -naphthylthiocarbamide.—Naphthylamine thiocyanate (obtained by double decomposition of the hydrochloride and potassium thiocyanate) is gradually transformed at 100° into the metameric thiocarbamide, which crystallises in white laminae (m. p. 180°).

Di- β -naphthylthiocarbamide, formed on boiling β -naphthylamine in alcoholic solution with excess of carbon bisulphide and a little potash, crystallises in white laminae (m. p. 193°).

β -Naphthylthiocarbimide, $C_{11}H_7NS$, is produced on distilling the last mentioned compound with phosphoric anhydride. It forms yellowish-white crystals (m. p. 62 — 63°), and when heated with alcoholic ammonia or naphthylamine it yields mono- or di-naphthylthiocarbamide.

β -Naphthylthiourethane is produced by the action of absolute alcohol on β -naphthylthiocarbimide at 130° . It forms yellowish crystals (m. p. 96 — 97°). With ammoniacal silver solution its alcoholic solution gives a white curdy precipitate of the composition $C_{13}H_{12}AgONS$, whence it is concluded that the constitutional formula of the substance is $C_{10}H_7N:C(SH).OEt$.

Mono- β -naphthylcarbamide is produced by the action of naphthylamine hydrochloride on urea at 150° . It crystallises in white matted needles (m. p. about 287°). J. R.

Action of Nitric Acid on Anthracene Dihydride and Ethylanthracene Dihydride. By C. LIEBERMANN and L. LANDSHOFF (*Ber.*, **14**, 467—475).—When colourless nitric acid (sp. gr. 1.4) diluted with an equal weight of glacial acetic acid is slowly added to finely divided anthracene dihydride suspended in well cooled glacial acetic acid, crystals of *hydroanthracene nitrite*, $C_6H_4 < \begin{smallmatrix} CH_2 \\ C(ONO)_2 \end{smallmatrix} > C_6H_4$, are slowly deposited. After leaving the mixture at rest for two days, the crystals are collected on a funnel. The mother-liquor afterwards deposits

dinitroanthrone, $C_{14}H_8N_2O_5$, which melts with decomposition at 116° . The hydroanthracene nitrite is purified by washing, first with glacial acetic acid and then with alcohol. It is dried on a porous plate, powdered, and dissolved in benzene at a temperature which must not exceed 40° . It is precipitated from this solution by light petroleum in colourless crystals, which melt with decomposition at 125° . This compound is isomeric with the body obtained by the action of nitrous fumes on anthracene. It is decomposed by boiling with an alkali, nitroso-oxanthranol and nitronitroso-anthrone being formed. The latter compound, $C_{14}H_8N_2O_4$, is insoluble in alkalis, but is deposited from an acetic acid solution in golden-yellow needles (m. p. 263). It is converted into anthraquinone by oxidation, and into anthranol by reduction.

Nitroso-oxanthranol, $C_6H_4 \left\langle \begin{array}{c} \text{CO} \\ \text{C(NO)(OH)} \end{array} \right\rangle C_6H_4$, is precipitated from its solution in alkalis by acids. It is easily decomposed by acids and by alcohol. The sodium salt crystallises in orange-coloured needles, which exhibit a silky lustre.

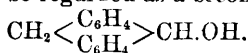
Ethylanthrahydride-nitrite, $C_6H_4 \left\langle \begin{array}{c} \text{CEt} \\ \text{ONO} \\ \text{C(ONO)}_2 \end{array} \right\rangle C_6H_4$, formed by the action of nitric acid on a solution of ethylanthradihydride in glacial acetic acid, is a crystalline compound melting at 130° with decomposition. It is also decomposed by hot acetic acid, with evolution of red fumes.

Ethylnitro-anthrone, $C_6H_4 \left\langle \begin{array}{c} \text{CEt} \\ \text{ONO} \\ \text{CO} \end{array} \right\rangle C_6H_4$, forms colourless crystals, which melt at 102° , and decompose at 130° . This substance is not attacked by dilute alkalis.

By the action of alcohol on ethylanthrahydride-nitrite at 120° , yellow needle shaped crystals of nitrosoanthrone (m. p. 135°) are produced; at 140° the nitrite is converted into ethyloxanthranol.

W. C. W.

Formation of Dihydroanthranol and of Anthracene from Anthraquinone. By H. R. v. PERGER (*J. pr. Chem.* [2], **23**, 137—146).—Anthraquinone reduced by potash and zinc-dust yields, according to Graebe and Liebermann, anthraquinol. According to the author, when anthraquinone is heated with zinc-dust and ammonia, the blood-red solution becomes light yellow, and an oily yellow mass separates, which solidifies on cooling. This, when exhausted with hot alcohol, yields first a white crystalline substance, afterwards anthranol and much anthracene. The white crystals dissolve in light petroleum spirit, and on cooling beautiful long silky needles separate (m. p. 76°). These are soluble in boiling water, but on prolonged boiling are decomposed, with formation of anthracene. These also gradually decompose when exposed to the air. Their composition corresponds with the formula $C_{12}H_{12}O = (C_{14}H_{10} + H_2O)$, and they may therefore be regarded as a secondary alcohol—



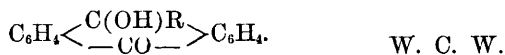
Heated with alkalis, the substance yields anthranol, $C_{14}H_{12}O - H_2 = C_{14}H_{10}O$. The author designates it as *dihydroanthranol*. Acetyl derivatives could not be obtained. Bromine acting on its solution in carbon bisulphide gives rise to a bromine derivative crystallising in yellow needles (m. p. $92-94^\circ$); it is very unstable. O. H.

Dinitroxyanthraquinone. By S. E. SIMON (*Ber.*, **14**, 464—467).—Monoxyanthraquinone is prepared by heating sodium anthraquinone-sulphonate with soda at $160-165^\circ$ for five hours. The solution of the fused mass is acidified with hydrochloric acid, boiled, and filtered. The precipitate is extracted with hot baryta-water, and the monoxyanthraquinone reprecipitated by an acid. After recrystallisation from alcohol, it is obtained in golden plates (m. p. 302°).

Dinitroxyanthraquinone, $C_{14}H_8(NO_2)_2(OH)O_2$, prepared by dissolving the preceding compound in 15 times its weight of warm nitric acid (sp. gr. 1.52), crystallises in pale yellow needles which are sparingly soluble in cold water, alcohol, ether, and benzene. The crystals melt at 276° with decomposition if cautiously heated, but explode when suddenly heated. When the compound is boiled with an aqueous solution of potassium acetate, *potassium dinitroxyanthraquinone*, $C_{14}H_8(NO_2)_2(OK)O_2$, is obtained in red scales, which are sparingly soluble in water. The silver salt crystallising in red needles, and the copper salt forming yellow needles containing 2 mols. H_2O , are sparingly soluble. The magnesium salt crystallises in orange-coloured needles, $[C_{14}H_8(NO_2)_2O_2.O]_2Mg + 5H_2O$, freely soluble in water.

On reduction with tin and hydrochloric acid, sulphuretted hydrogen or sodium sulphide, dinitroxyanthraquinone yields a mixture of two crystalline compounds which can be separated by the difference of their solubilities in alcohol. The more soluble product dissolves in alkalis, forming a blue solution, the less soluble produces a violet liquid. W. C. W.

Alkyloxanthranols. By C. LIEBERMANN (*Ber.*, **14**, 452—455).—The formation of alkyloxanthranols by the oxidation of an acetic acid solution of alkylanthracenedihydrides by chromic acid in the cold, has caused the author to change his views on the constitution of the former compounds. He now considers it probable that the alcoholic radicle in an alkyloxanthranol is attached to one of the middle carbon atoms, and not to the oxygen atom, thus:



Derivatives of Ethyl-, Amyl-, and Methyl-oxanthranols. By C. LIEBERMANN and L. LANDSHOFF (*Ber.*, **14**, 455—462).—Methyl-, ethyl-, and butyl-oxanthranol were prepared according to the process previously described (*Ber.*, **13**, 1599, and this vol., 100), with the exception that an alcoholic bromide was substituted for the iodide. Amyloxanthranol is best prepared by boiling the following mixture in a flask, fitted with an upright condenser: 120 grams of anthra-

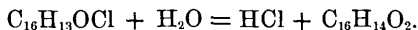
quinone moistened with alcohol, 180 grams of solid potash, 250 grams of zinc-dust, 100 grams of amyl bromide, and 5 litres of water. After boiling for 12 hours, the excess of amyl bromide is distilled off, and the remaining liquid shaken with air until colourless and then filtered. Amyloxanthranol is extracted from the residue with warm alcohol: it is precipitated from the concentrated alcoholic extract by water, then dried and dissolved in a small quantity of benzene. On the addition of light petroleum to this solution, amyloxanthranol crystallises out. Ethyloxanthranol can also be purified by precipitation from its benzene solution by light petroleum.

Methyloxanthranol is less soluble in warm alcohol than its homologues, and consequently its purification is more difficult. The mixture of methyloxanthranol and unaltered anthraquinone, which is extracted on treating the crude product with hot alcohol, is boiled with dilute soda and zinc-dust until the anthraquinone is completely removed. On recrystallising the residue from benzene, methyloxanthranol is obtained in fluorescent crystals (m. p. 187°). It forms anthracene-dihydride when acted on by phosphorus and hydriodic acid, and it is not attacked by phosphorus pentachloride.

Amylanthradihydride, prepared from amyloxanthranol by the process previously described, boils with partial decomposition at 350° . Its sp. gr. at 18° is 1.031. *Ethylanthradihydride* boils at 320° , and has a sp. gr. of 1.049 at 18° . These hydrocarbons are quantitatively converted into the corresponding oxanthranols, by oxidation with chromic acid solution in cold glacial acetic acid.

When ethyloxanthranol is mixed with phosphorous pentachloride (equal molecules) an active reaction takes place. The liquid product is diluted with light petroleum and filtered. On evaporating the filtrate, *ethyloxanthranol chloride*, $C_{16}H_{13}ClO$, is deposited in rhombic crystals, which melt at 89° , and at a higher temperature evolve hydrochloric acid.

Amyloxanthranol chloride, $C_{19}H_{19}ClO$, also forms rhombic crystals (m. p. 85°). These chlorides are decomposed by boiling water or alcohol, forming hydrochloric acid and the oxanthranol—



The compound $C_{19}H_{14}O$, obtained by the action of strong sulphuric acid on amyloxanthranol yields, on oxidation with chromic acid in an acetic acid solution, anthraquinonecarboxylic acid, and a crystalline body (m. p. 157°), soluble in alcohol. On reducing the compound, $C_{19}H_{14}O$, in glacial acetic acid solution, with amorphous phosphorus and hydriodic acid, it yields a hydrocarbon, $C_{19}H_{18}$, which crystallises in colourless needles (m. p. 92°), and resembles triphenylmethane in some respects.

W. C. W.

Butyloxanthranol. By C. LIEBERMANN and WALDER (*Ber.*, **14**, 462—464).—*Butyloxanthranol*, $C_6H_4 < \frac{C(OH)(C_4H_9)}{CO} > C_6H_4$, crystallises in needles and prisms (m. p. 130°). *Butylanthradihydride* is a fluorescent oil, which is oxidised to anthraquinone by boiling with chromic acid. At the ordinary temperature, chromic acid converts an

acetic acid solution of the dihydride into butyloxanthranol. *Butyloxanthranol chloride* crystallises in plates (m. p. 78°). It is not attacked by ammonia gas at the ordinary temperature, but is decomposed by boiling water, forming hydrochloric acid and butyloxanthranol.

W. C. W.

Researches on Glucosides. By H. SCHIFF (*Gazzetta*, **11**, 99—113).—This paper consists of four sections, abstracts of the last three of which have already appeared (this vol., 180, 439, and 439). The first section is on

The Constitution of Arbutin.—An examination of some residues from the preparation of arbutin by Piria, found in the collection of the Turin Laboratory, showed that the substance consisted of a mixture of two compounds. The nearly black mass, purified by precipitation with lead subacetate and removal of the excess of lead by hydrogen sulphide, was submitted to careful fractional crystallisation, the elementary composition, melting point, and water of crystallisation being determined in each fraction. Each fraction (dried at 115°) showed two melting points, a part melting at about 141 — 145° , the remainder at 161 — 165° ; tables are given of the melting points and elementary composition of each successive fraction, from which it is clearly seen that they are mixtures in various proportions of arbutin, $C_{12}H_{16}O_7$ (m. p. 165 — 166), with methylarbutin, $C_{13}H_{18}O_7$ (m. p. 141 — 145°). The results of this examination render it evident, as formerly suggested by Fittig, that the compound examined by Hlasiwetz and Habermann, and to which they assigned the formula $C_{23}H_{34}O_{11}$, was really a mixture of arbutin with methylarbutin, and was probably a second crop of crystals from a preparation on a large scale.

Pure arbutin, prepared by fractional crystallisation of a preparation purchased some years ago from Trommsdorf, crystallises in long silky needles of the composition $C_{12}H_{16}O_7$, and melting at 165 — 166° , but when heated a second time it melts at 187.5° .

It is an interesting question in vegetable physiology as to whether arbutin and methylarbutin are invariably associated in the plant, or whether the latter occurs only under particular conditions.

C. E. G.

Aesculetin. By C. LIEBERMANN and H. MASTBAUM (*Ber.*, **14**, 475—478).—A determination of the amount of hydrobromic acid evolved when bromine is added to a glacial acetic acid solution of aesculetin, proves that the product is $C_9H_3Br_3O_4$, and not an addition-product, $C_9H_5Br_3O_4$.

When the compound of para-aesculetin and sodium sulphite is moistened with water and exposed to the vapour of ammonia, it acquires a blue colour. In presence of ammonia, the aqueous solution gives with lead acetate, a blue precipitate, from which sulphuretted hydrogen precipitates the lead, leaving a colourless solution which turns blue on addition of soda. On the addition of a minute quantity of an alkali to a solution of the original colouring matter, an intense vermilion coloration is produced.

W. C. W.

Curcumin. By C. L. JACKSON (*Ber.*, **14**, 485—487).—Curcumin is obtained from Bengal turmeric root by extraction with ether, the oil

having been previously removed by treatment with carbon bisulphide. The residue which remains when the ethereal extract is evaporated, is purified by washing with cold, and crystallising from hot alcohol. Curcumin crystallises in yellow prisms (m. p. 178°). Analyses of the compound give numbers agreeing with the formula $C_{28}H_{26}O_8$, whilst Daube (*Ber.*, **3**, 609), finds $C_{10}H_{10}O_3$, and Grajewsky (*Ber.*, **3**, 624; **5**, 1103, this Journal, 1873, 504), and Kachler (*Ber.*, **3**, 713), give $C_{16}H_{16}O_4$.
W. C. W.

Hæmateïn. By. W. HALBERSTADT and M. A. v. REIS (*Ber.*, **14**, 611—612).—The authors have succeeded in obtaining hæmateïn by exhausting fermenting logwood with ether; its composition is $C_{16}H_{16}O_6$, a formula which agrees most nearly with those of Erdmann and Reim. Hæmateïn forms red metallic-like crystals, which are sparingly soluble in water and alcohol, insoluble in benzene; it is very stable, and can be heated to 200° C. without decomposition. The authors, however, were unable to obtain hæmateïn from logwood extract of commerce.

V. H. V.

Pyridene and Methylpyridine-carboxylic Acids. By S. HOOGWERFF and W. A. v. DORP (*Ber.*, **14**, 645—647).—The authors have obtained methylpyridinedicarboxylic acid as a product of the oxidation of lepidin, and they propose to name it provisionally *methylquinolinic acid*.

This acid crystallises in tables or prisms, sparingly soluble in cold water, alcohol, and ether, more easily soluble in hot water. With acid aqueous solution, ferrous sulphate gives a golden colour, lead and barium acetate white precipitates, cupric acetate a clear blue precipitate. The neutral silver salt is also very characteristic. Two acid potassium salts, $C_8H_8NO_4K + 3Aq$ and $C_8H_8NO_4K + 2Aq$, were obtained.

By heating methylquinolinic acid to 160—167° it is decomposed into carbonic anhydride and *methylpyridinemonoxycarboxylic acid*, which crystallises from alcohol in needles (m. p. 209—210°), easily soluble in hot water and alcohol. An aqueous solution of this acid gives crystalline precipitates with silver nitrate and cupric acetate.

Methylpyridinemonocarboxylic acid is oxidised by potassium permanganate to a pyridinedicarboxylic acid, crystallising in needles (m. p. 250°), identical with cinchomeronic acid. The author's methylquinolinic acid is identical with König's, but isomeric with Böttinger's.

The author does not agree with Skraup's view that, accepting Körner's formula for pyridine, the carboxyl groupings are in the positions $N : COOH : COOH = [1 : 2 : 3]$, but rather in the position $[1 : 2 : 5]$, if it be supposed that quinolinic acid has the groupings in the positions $[1 : 2 : 3]$; for there are three pyridinedicarboxylic acids, which yield γ -pyridinecarboxylic acid, viz., cinchomeronic, lutidinic, and Böttinger's pyridinedicarboxylic acid. Similarly there are three dicarboxylic acids, which yield nicotinic acids, viz., cinchomeronic, quinolinic, and isocinchomeronic. But the 1 : 4 pyridinemonocarboxylic acid is characterised by yielding only two dicarboxylic acids, so that it cannot be either γ -methylpyridinecarboxylic or nicotinic acid. If then quinolinic acid has the groupings in the

position [1 : 2 : 3], cinchomeric acid must have the groupings in the positions [1 : 2 : 6], for it yields a mixture of γ -pyridinecarboxylic and nicotinic acids.

V. H. V.

Synthetic Picoline-monocarboxylic and Pyridine-dicarboxylic Acids. By C. BÖTTINGER (*Ber.*, **14**, 67—70).—When uvitonic acid is heated in an oil-bath at 240° , it breaks up almost entirely into carbonic anhydride and a substance which the author calls picolinecarboxylic acid. This acid dissolves in hot water and crystallises therefrom in oblique prisms. Heated on a watch-glass, it volatilises entirely without melting. The aqueous solution gives precipitates with silver and copper salts. Picoline-carboxylic acid dissolves easily in acids, forming definite salts. The hydrochloride, $C_7H_7NO_2 \cdot HCl$, crystallises in brilliant prisms.

Pyridine-dicarboxylic acid is the name given to a body formed by the oxidation of picolinecarboxylic acid with potassium permanganate. This acid dissolves in hot water and crystallises from the solution in roundish warty masses. It gives precipitates with barium, calcium, lead, and silver salts. The silver salt, $C_7H_5Ag_2NO_4 + 2H_2O$, is a white flocculent precipitate, easily soluble in ammonia.

J. R.

Fractional Distillation of Crude Quinoline: Oxidation-products of Lutidine. By O. DE CONINCK (*Bull. Soc. Chim.* [2], **35**, 296—303; compare this vol., p. 443).—2.9 kilos. crude quinoline, obtained by distilling 1 part cinchonine with 3 parts solid potash, until dense white fumes appeared, were subjected to careful fractional distillation. Above 160° , the proportion of pyridic bases in the different fractions increased, but about 225° the pyridic odour became much less distinct, and was replaced by the more penetrating and disagreeable odour of the quinoline bases. With a little practice, it is easy to recognise the odour peculiar to each base. Lutidine boiling at 166° , and two collidines boiling at 180° and 195° respectively, were present in about equal quantities, whilst the amount of parvoline obtained was about half that of the lutidine. After each rectification, the operator suffered from a violent headache, sometimes accompanied by giddiness; these symptoms generally disappeared on breathing the fresh air. The crude quinoline gave off ammonia as soon as it was heated, and began to boil at 90° . Fraction 90 — 110° consisted mainly of an aqueous solution of methylamine, a body which is also formed by the action of potash on caffeine and codeine. Fractions 110 — 130° , 130 — 160° , and 160 — 175° contained two lutidines, one boiling at 130 — 160° and forming a golden-yellow platinochloride, the other boiling at 165° and forming an orange-red platinochloride. Neither pyridine, picoline, nor pyrroline was obtained.

The lutidine boiling at 165° , when oxidised by means of potassium permanganate, gave nicotinic acid, and would therefore appear to be ethylpyridine, as Wischnegradsky supposed. On the other hand, it may possibly be ortho-dimethyl-pyridine, in which one of the methyl groups is more easily oxidised than the other, and is separated as formic acid.

C. H. B.

Hydroxyquinoline. By K. BEDALL and O. FISCHER (*Ber.*, **14**, 442—443).—Quinolinesulphonic acid is a crystalline, not an amorphous compound, but in other respects it agrees with Lubavin's (*Ber.*, **2**, 400) description of its properties. An excellent yield of hydroxyquinoline is obtained by fusing the sulphonic acid with three times its weight of soda. Sulphuric acid is added to the aqueous solution of the fused mass until the liquid becomes turbid; after a short interval long needle-shaped crystals (m. p. 75°) of hydroxyquinoline are deposited. This compound appears to be identical with *quiniphenol*, which Weidel (*Monatshft. Wien. Akad.*, 1880) obtained from cinchoninesulphonic acid. W. C. W.

Action of Sodium on Quinoline. By C. G. WILLIAMS (*Chem. News*, **43**, 145—147).—Quinoline when boiled with sodium becomes polymerised, yielding *diquinoline*, a yellow oil, which forms a crystalline hydrochloride of a splendid red colour. The liquid obtained by the reaction, after treatment with hydrochloric acid and separation of the crystalline diquinoline hydrochloride, is fractionally precipitated with platinum chloride, when it yields four precipitates.

Precipitate.	Per cent. Pt.	Agreeing with formula.	Per cent. Pt.
I	22.59	$2(C_{18}H_{14}N_2)HCl, PtCl_4$	22.18
II	23.83		
III	28.30	$C_{18}H_{14}N_2, 3HCl, PtCl_4$	28.00
IV	28.59	$C_{18}H_{14}N_2, 2HCl, PtCl_4$	29.51

No. II is probably a mixture of Nos. I and III, although the formula $2(C_{18}H_{14}N_2), PtCl_4$ requires 23.18 per cent. platinum. However, the formation of such a body in the presence of free hydrochloric acid is improbable.

Action of Sodium-amalgam.—When quinoline is treated, first in the cold and then over a water-bath, with sodium-amalgam (10 per cent. Na), it yields diquinoline hydrochloride and a small quantity of a yellow precipitate almost insoluble in water. A large proportion of the quinoline, however, is unacted on; this, on further treatment with sodium-amalgam (10 of base to 30 amalgam), yields only a small quantity of the scarlet hydrochloride and a solid resinous base of yellow colour. The hydrochloride of this base, fractionally precipitated with platinum chloride, yields the compound $2(C_{18}H_{14}N_2), 4HCl, PtCl_4$, and a mixture of other platinochlorides, but in too small quantities for analysis.

The solid base melts to a yellow oil, having an odour of quinoline. At a red heat, it boils away and partially carbonises. Nitric acid dissolves the base with a reddish-brown colour: the solution is precipitated by water, and turned red by ammonia, in which the precipitate is soluble.

Diquinoline Platinochloride.—On adding platinum chloride to a boiling aqueous solution of diquinoline hydrochloride, a cadmium-yellow precipitate is obtained containing 24.54 per cent. of platinum. The filtrate from this precipitate, on cooling, deposits needles containing 35.7 per cent. platinum; $C_{18}H_{14}N_2, PtCl_4$ requires 33.11 Pt; $(C_{18}H_{14}N_2), 2HCl, PtCl_4$

requires 33.66. Of these two formulæ the latter is more probably that of the needles, owing to the presence of excess of hydrochloric acid in their formation.

All the numbers are given with reserve and open to correction, the subject being still under investigation. L. T. O'S.

Formation of Pyrroline. By C. BÖTTINGER (*Ber.*, **14**, 48).—A base having the properties of pyrroline is obtained, together with ammonia and ammonium carbonate, by heating calcium amidoglyoxalate. The same base is formed in large quantity, on heating a mixture of soda-lime and the calcium salt of a condensation-product of ammonium amidoglyoxalate previously described by the author (*Annalen*, **198**, 218). J. R.

Caffeine. By E. FISCHER (*Ber.*, **14**, 637—644).—In order to decide between the constitutional formulæ for caffeine proposed by Medicus and by Strecker, the author has examined the conversion of a caffeine into tetramethylalloxantin. For this purpose, he has endeavoured to build up dimethylalloxan systematically from bromocaffeine, and has examined this latter compound and its derivatives.

Bromocaffeine, $C_8H_5BrN_4O_2$, forms white crystals (m. p. 206°) sparingly soluble in water and alcohol, moderately soluble in hot acetic and hydrochloric acids: on heating with ammonia, it is converted into the corresponding amido-compound, $C_8H_5NH_2N_4O_2$. Bromocaffeine is formed from it by the action of alcoholic potash.

Ethoxycaffeine, $C_8H_5N_4O_2.OEt$ (m. p. 140°), is easily soluble in hot alcohol, sparingly soluble in water and ether. On heating a hydrochloric acid solution of ethoxycaffeine, it is decomposed into ethyl chloride and *hydroxycaffeine*, $C_8H_5N_4O_2.OH$, which crystallises in white needles (m. p. 350°), sparingly soluble in water, soluble in alkalis. It is easily distinguishable from caffeine by its strongly acid reaction. By the action of bromine on hydroxycaffeine, a dibrom-hydroxycaffeine is formed; this was not isolated, but converted directly by alcohol into *diethoxyhydroxycaffeine*, $C_8H_5N_4O_2(OEt)_2.OH$, which crystallises in prisms (m. p. $195-205^\circ$), sparingly soluble in water, easily soluble in hot alcohol and alkalis. An analogous compound, methoxyethoxyhydroxycaffeine, may be obtained in the form of colourless crystals (m. p. 178°). By heating the ethyl or the methyl compound with hydrochloric acid, apocaffeine is formed, thus: $C_8H_5N_4O_2(OEt)_2.OH + 2H_2O = C_7H_7N_3O_5 + MeNH_3 + 2EtOH$.

Apocaffeine, $C_7H_7N_3O_5$, crystallises in prisms (m. p. 147°), soluble in hot water and alcohol. By boiling in aqueous solution, it is decomposed into carbonic anhydride and *hypocaffeine*, $C_6H_7N_3O_5$, which forms colourless crystals (m. p. 181°), decomposed by baryta-water into ammonia, methylamine, and an oxalate, thus: $C_6H_7N_3O_5 + 4H_2O = C_2H_2O_5 + CO_2 + 2MeNH_2 + NH_3$. The author considers that the constitutional formula of Medicus for caffeine is the more probable.

By the action of bromine on the bromine, it is converted into a monobromo-compound, $C_7H_7N_4O_3Br$ (m. p. 310°), which has all the characters of an acid, is insoluble in alkalis, and can be reprecipitated by acids unchanged. V. H. V.

Constitution of some Alkaloids of Cinchona Bark. By O. HESSE (*Annalen*, 205, 314—359).—1. *Action of Acetic Anhydride on the Cinchona Alkaloids.*—Wright and Beckett (this Journal, 1876, 1, 655) found that acetic anhydride acting on quinine and conquinine produces acetyl-quinicine, while on cinchonidine and cinchonine it produces acetyl-cinchonicine, the alkaloids suffering an internal change. The author finds that the acetyl-derivatives may be produced by treating the alkaloids or their hydrochlorides or sulphates with acetic anhydride at 60° or 80°. The formation of the acetyl-derivative is complete after a few hours.

With the exception of acetyl-quinine, all these compounds are amorphous. They can be dried at 100° without decomposition, and on boiling, or on long standing at the ordinary temperature with alcoholic potash, are decomposed into acetic acid and the original alkaloid.

The acetyl compounds are readily soluble in dilute acids, and are thrown down from these solutions as resinous precipitates by alkalis. Their alcoholic solutions are bitter, and have an alkaline reaction, the acetyl-quinine and acetyl-conquinine solutions giving green colorations, with chlorine and ammonia, the solutions of the other acetyl compounds, like the original substances, not giving this reaction.

	M. p. (uncorr.)	In 97 p. c. alcohol. $t = 15^\circ$ $p = 2$ $[\alpha]_D$.	In $H_2O + 3HCl$ $t = 15^\circ$ $p = 2$ $[\alpha]_D$.	Platinum salt.	Gold salt.
Acetyl-quinine ..	108°	— 54·3°	— 114·8°	Dark yellow, amorphous	Fiery yellow
Acetyl - conquinine.	—	+ 127·6	+ 158·6	Amorphous.	Fine yellow, amorphous
Acetyl-cinchonidine.	42°	— 38·4	— 81·3	Yellow.....	Fine yellow, amorphous
Acetyl-homocinchonidine.	—	— 34·0	— 72·5	Orange yellow, amorphous	Fine yellow, amorphous
Acetyl - cinchonine.	—	+ 114·1	+ 139·5	Orange red, crystalline	Yellow, amorphous

2.—*Action of Hydrochloric Acid (sp. gr. 1·125) on the Cinchona Alkaloids.*—It was found that these alkaloids could not resist the action of this acid when heated in sealed tubes at 140—150° for 6—10 hours, decomposition taking place, and in the case of quinine and conquinine, methyl chloride being produced.

By this reaction—

Quinine	yields	Apoquinine and Methyl chloride.
Conquinine	„	Apoconquinine and Methyl chloride.
Cinchonidine	„	β -Cinchonidine and Apocinchonidine.
Homocinchonidine	„	Apocinchonidine.
Cinchonine	„	Apocinchonine and Diapocinchonine.

No other bodies produced by this reaction could be recognised.

	Melts at (uncorr.)	Rotatory power on polarised light.	
		In 97 per cent. alcohol solution. $p = 2$ $t = 15^\circ$ $[\alpha]_D$.	In $H_2O + 3HCl$. $p = 2$ $t = 15^\circ$ $[\alpha]_D$.
Apoquinine	160°	- 178.1°	- 246.6°
Apoconquinine	137	+ 155.3	+ 216.5
Apocinchonidine	225	- 129.2° [$p = 0.8$]	- 160.2 (fr. cinchonidine) - 160.4° (fr. homocinchonidine)
Apocinchonine	209	$\times 160.0$ [$p = 1$]	+ 212.3°
Diapocinchonine	—	+ 20°	+ 23.6

Apoquinine, $C_{19}H_{22}N_2O_2$, is completely amorphous, with a bitter taste and an alkaline reaction. Readily soluble in ether, alcohol, and chloroform, slightly in cold water, and easily in hot. Ammonia and soda dissolve the fresh precipitate pretty easily, but with difficulty when air-dried. No fluorescence in an acid solution of sulphuric acid, but an alcoholic solution is coloured slightly greenish-yellow on addition of chlorine and ammonia. The air-dried alkaloid retains 2 mols. H_2O , a small portion of which is lost by prolonged exposure to dry air. It completely neutralises acids. The neutral and acid hydrochlorides are amorphous, and soluble in alcohol and water. The neutral tartrate is an oily mass, easily soluble in cold water. The platinochloride is a yellow flocculent precipitate, fairly soluble in dilute hydrochloric acid, but only slightly in cold water. Composition, $C_{19}H_{22}N_2O_2, PtCl_6H_2 + 3H_2O$. The aurochloride is a reddish-yellow resin.

Apoconquinine resembles apoquinine both outwardly and in composition, but it is extremely difficult to obtain a non-effloresced hydrate. Apoconquinine is a white amorphous powder readily soluble in alcohol and ether with alkaline reaction, and giving a green coloration on the addition of chlorine and ammonia to its alcoholic solution. Its acid solution in sulphuric acid, however, shows no fluorescence. Ammonia or soda solution throws it down as a white bulky flocculent precipitate, soluble with difficulty in excess. With hydrochloric acid it forms a neutral salt, crystallising in needles, and readily soluble in water or dilute hydrochloric acid.

Potassium iodide and thiocyanate solutions at first produce milky, and after a time resinous precipitates. The platinochloride is a fine yellow amorphous flocculent precipitate, of the composition $C_{19}H_{22}N_2O_2, PtCl_6H_2 + 3H_2O$.

Apocinchonidine, $C_{19}H_{22}N_2O$, is obtained under like conditions from homocinchonidine and from cinchonidine. When cinchonidine is

employed, and is heated with hydrochloric acid for six hours only, some β -cinchonidine is formed, which however by further heating is also converted into apocinchonidine. Apocinchonidine being very sparingly soluble in highly dilute alcohol, is readily obtained pure. It crystallises from strong hot alcohol in small shining plates, sparingly soluble in ether and chloroform, and almost insoluble in cold water. Its alcoholic solution has an alkaline reaction. Readily soluble in dilute acids, from which ammonia and soda throw it down as a white amorphous flocculent precipitate, which after a time becomes crystalline. No fluorescence. Bitter taste in solution. Sodium potassium tartrate produces a resinous precipitate only when the solution is saturated with it, disappearing on addition of water. The neutral hydrochloride and neutral sulphate are amorphous, and readily soluble in water and alcohol. The platinochloride, $C_{19}H_{22}N_2O \cdot PtCl_6H_2 + 2H_2O$, is at first a flocculent, but later a crystalline precipitate, sparingly soluble in water.

Apocinchonine, $C_{19}H_{22}N_2O$, crystallises anhydrous, is readily soluble in acids, and is precipitated flocculent by alkalis, but ultimately becomes crystalline. It crystallises in colourless prisms, sparingly soluble in ether and chloroform, rather more so in alcohol, especially on boiling; insoluble in water. Its alcoholic solution has a bitter taste and alkaline reaction. By dissolving it in an equivalent weight of sulphuric acid, with some water, and evaporating to dryness, the residue turns brown even at 120° , but at from 130° to 140° the alkaloid changes completely without loss of weight into apocinchonicine.

Apocinchonicine completely neutralises acids, forming beautifully crystalline salts. The neutral sulphate forms tufts of delicate needles, readily soluble in alcohol, chloroform, and hot water, slightly in cold water.

The neutral hydrochloride is obtained in concentrically grouped silky needles, very easily soluble in alcohol and water. The platinochloride, $C_{19}H_{22}N_2O \cdot PtCl_6H_2 + 2H_2O$, is an amorphous flocculent dark-red precipitate.

Diapocinchonine, $C_{38}H_{44}N_4O_2$, remains dissolved in the mother-liquor of the apocinchonine. Readily soluble in ether, alcohol, and chloroform. Its alcoholic solution has an alkaline reaction. Excess of ammonia or soda solution precipitates the alkaloid from its hydrochloric acid solution as a resin. It forms neutral and acid salts with acids. The neutral oxalate is amorphous, scarcely hygroscopic, and readily soluble in chloroform. The neutral hydrochloride is likewise amorphous, and readily soluble in water. The platinochloride, $C_{38}H_{44}N_4O_2 \cdot 2PtCl_6H_2 + 4H_2O$, is a yellow amorphous flocculent precipitate. The aurochloride, $C_{38}H_{44}N_4O_2 \cdot 4AuCl_4H + 2H_2O$, is a beautiful yellow amorphous precipitate, slightly soluble in water and dilute acids. Diapocinchonine is formed from apocinchonine by the prolonged action of hydrochloric acid. It is distinct from cinchonine, apocinchonicine, and the naturally-occurring dicinchonine (*Ber.*, 10, 2156).

3. *Action of Acetic Anhydride on the above-described Apo-bases.*—The acetyl-derivatives of the apo-bases were readily obtained by dissolving the pure bases (dried at 100°) in an excess of acetic anhydride

allowing them to stand at 60° to 80° for a few hours, and then evaporating them at the same temperature after the addition of water. Slightly yellow amorphous products were obtained, which could be dried at 100°, became brittle on cooling, and with the exception of the acetyl-diapocinchonine produced white powders on pulverisation. Readily soluble in ether, chloroform, and alcohol; bitter taste; slight alkaline reaction. Very slightly soluble in water, but readily in dilute hydrochloric acid, whence precipitated as resins by ammonia and soda solutions. The apoquinine and apoconquinine derivatives give blue fluorescent solutions with sulphuric acid, and their alcoholic solutions give intense dark-green colorations with chlorine and ammonia, but the others have neither of these properties. The bodies are decomposed by boiling with alcoholic potash, with formation of potassium acetate and the apo-bases.

	M. p.	$p = 2, t = 15^{\circ}$			
		In 97 p. c. alcohol. [α] _D .	In H ₂ O + 3HCl. [α] _D .		
Diacetylapoquinine	—	— 61·8°	— 107·5°	Dark yellow, flocculent, becoming crystalline	Fine yellow, amorphous, flocculent.
Diacetylapoconquinine	60°	+ 40·4	+ 78·4	Do. do.	—
Acetyl apocinchonidine	—	— 61·8	— 87·9	Do. do.	Do. do.
Acetyl apocinchonine	—	+ 71·4	+ 97·9	Light yellow	—
Diacetyldiapocinchonine	—	0	+ 26·1	Orange yellow	Do. do.
				Do. do.	

4. *Action of Concentrated Hydrochloric Acid (saturated at -17°) on the above-mentioned Apo-bases and the Original Alkaloids respectively.*—On heating the primary apo-bases, apoquinine, apocinchonidine, and their isomerides for six hours in sealed tubes at 140° or 150°, they are converted, with absorption of hydrochloric acid, into hydrochloro-apo-compounds, in which in all cases 1 mol. of the base contains 3 mols. HCl, of which, however, only 2 mols. are acted on by silver nitrate. On mixing the contents of the tube with half its volume of water, most of these compounds separate out. Diapocinchonine is unacted on by this treatment. The original alkaloids give the same products as the apo-bases: hence Zorn's compounds (*J. pr. Chem.* [2], 8, 279) were not immediate derivatives of the alkaloids, but were derived from the apo-compounds by addition of 1 mol. of hydrochloric acid.

The hydrochloro-apo-bases all rotate a ray of polarised light, some to the right, but others to the left. Their properties are described in

some detail. By the action of acetic anhydride, the diacetyl derivatives of hydrochlor-apoquinine and hydrochlor-apoconquinine were obtained; the other bases gave monacetyl derivatives.

The author concludes that this investigation has undoubtedly shown the presence of one hydroxyl-group in quinine, cinchonidine, and its isomerides capable of being exchanged for acetyl. These hydroxyl-groups were still present in the hydrochlorapo-bases; hence Zorn's statement that in them hydroxyl is substituted by chlorine is incorrect.

F. L. T.

Methyl- and Ethyl-derivatives of Quinine. By A. CLAUS and F. MALLMANN (*Ber.*, **14**, 76—80).—*Quinine methiodide*, $C_{20}H_{24}N_2O_2 \cdot CH_3I$, formed on mixing molecular proportions of quinine and methyl iodide both in ethereal solution, and allowing the mixture to stand for some days, crystallises in colourless needles easily soluble in hot water and alcohol. The crystals melt at $233-236^\circ$, undergoing decomposition. They dissolve in warm dilute hydrochloric acid, forming an intense yellow solution, which as it cools deposits yellow crystals, probably $C_{20}H_{24}N_2O_2 \cdot MeI \cdot HCl$.

Quinine methylbromide, obtained either in the same manner as the preceding compound or indirectly from it, forms delicate silky needles melting at $124-126^\circ$.

Quinine methylchloride, obtained by decomposing the iodide with silver nitrate and adding sodium chloride to the filtrate, crystallises in long delicate silky needles (m. p. $181-182^\circ$). It forms a crystalline platinochloride.

Quinine dimethiodide, $C_{20}H_{24}N_2O_2 \cdot (MeI)_2$, is obtained either by heating quinine with 2 mols. of methyl iodide in sealed tubes, or by boiling an alcoholic solution of quinine methiodide with methyl iodide. It crystallises generally in small tables, but sometimes in other forms, and with varying proportions of water.

Quinine meth-ethiodide, $C_{20}H_{24}N_2O_2 \cdot MeI \cdot EtI$, is obtained by boiling together molecular proportions of ethyl iodide and quinine methiodide in alcoholic solution. It crystallises in thin golden-yellow laminae, which turn brown in the light.

Quinine ethomethiodide, $C_{20}H_{24}N_2O_2 \cdot EtI \cdot MeI$, crystallises in beautiful pale-yellow prisms. It is isomeric with the preceding compound, and is obtained in a similar manner, but is far more stable.

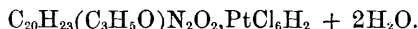
Methylquinine, $C_{20}H_{23}MeN_2O_2$, obtained by boiling quinine methiodide with potash or baryta-water, is a pale-yellow oily body of extremely bitter taste, gradually turning brown in the light. It dissolves readily in acids, but does not form crystallisable salts. The solution in excess of sulphuric acid is not fluorescent. The platinochloride, isomeric with that of quinine methylchloride, is a yellow indistinctly crystalline precipitate, decomposed by dilute hydrochloric acid. The aurochloride is a very unstable yellow powder.

Methylquinine methiodide, $C_{20}H_{23}MeN_2O_2 \cdot MeI$, is formed when an alcoholic solution of methylquinine is mixed with methyl iodide. It crystallises in colourless needles, closely resembling those of quinine methiodide.

J. R.

Propionylquinine. By O. HESSE (*Annalen*, **205**, 358—359).—Obtained by treating quinine hydrochloride for several hours at 60° to 80° with propionic anhydride, then adding water and evaporating, dissolving residue in water, adding ammonia, and shaking with ether. On evaporating the ethereal solution, prisms are obtained embedded in a glutinous mass, which may be purified by pressing between blotting paper moistened with ether.

Propionylquinine, $C_{20}H_{23}(C_3H_5O)N_2O_2$, forms large colourless six-sided prisms of the rhombic system (m. p. 129°, uncorr.). Ether, alcohol, and chloroform dissolve it readily, but water only sparingly. The alcoholic solution has a bitter taste and an alkaline reaction, and is coloured intensely green by chlorine and ammonia. Alcoholic potash decomposes it on boiling, with production of quinine and propionic acid. The solution of the base in an excess of dilute sulphuric acid has a blue fluorescence, but the solution in hydrochloric acid has not. The latter solution, with $p = 2$ and 3 mols. HCl, when $t = 15^\circ$, gives $[\alpha]_D = -108.8^\circ$. Ammonia or alkalis produce resinous precipitates in the hydrochloric acid solution. Platinic chloride produces a dark-yellow amorphous flocculent precipitate, soon changing into splendid dark orange-coloured prisms,



The aurochloride, $[C_{20}H_{23}(C_3H_5O)N_2O_2, 2AuCl_4H + 2H_2O]$, is obtained in a similar manner as a fine yellow precipitate, which is amorphous at first, but appears to become crystalline later; it is almost insoluble in water. No trace of a quinicine derivative was formed.

F. L. T.

Tolyl-quinines. By A. CLAUS and C. BOTTLER (*Ber.*, **14**, 80—82).—By boiling quinine hydrochloride with para- and ortho-toluidine, the authors have obtained four new bases, α - and β -para-tolylquinine, and α - and β -orthotolylquinine. The α -compounds are chiefly produced when the heating is not prolonged beyond six hours. After 60 hours' heating, the products are almost exclusively β -compounds. The α -bases are oily bodies soluble in ether. The β -bases are amorphous, yellow, or brown powders insoluble in ether, soluble in chloroform and alcohol. All four bases form with platinic chloride yellow crystalline compounds having the formula

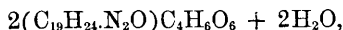


Cinchonidine. By A. CLAUS (*Ber.*, **14**, 413—416).—A reply to Hesse's remarks (*Ber.*, **14**, 45) on the existence of homocinchonidine.

W. C. W.

Cinchotine (Hydrocinchonine of Caventou and Willm). By C. FORST and C. BÖHRINGER (*Ber.*, **14**, 436—438).—Cinchotine, obtained by the oxidation of commercial cinchonine by Caventou and Willm (*Annalen*, Supp., **7**, 378), bears a close resemblance to pure cinchonine. The *sulphate*, $2(C_{19}H_{24}N_2O)SO_4H_2 + 12H_2O$, crystallises in hexagonal prisms. The *nitrate*, $C_{19}H_{24}N_2O.NO_3H + H_2O$, forms transparent plates. The *hydrochloride*, $C_{19}H_{24}N_2O.HCl + 2H_2O$, crystallises in slender needles. The *acid hydrochloride*, $C_{19}H_{24}N_2O.2HCl$,

is sparingly soluble in alcohol. The normal *hydrobromide* contains 2 mols. of water; the acid salt is anhydrous. The *tartrate*,

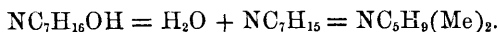


forms needle-shaped crystals, freely soluble in water; and the *thiocyanate*, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}.\text{HCNS}$, also crystallises in needles, which are sparingly soluble in cold water, and insoluble in a concentrated solution of potassium thiocyanide. W. C. W.

Action of Heat on Amines. By A. W. HOFMANN (*Ber.*, 14, 659—669).—The author, by following out the lines of his former experiments (*Ber.*, 14, 494) on the decomposition by heat of the amines, endeavours to throw some light on the constitution of piperidine.

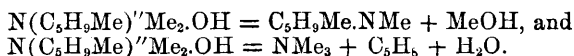
Methylpiperidine.—The author, by the distillation of methylethylpiperidine hydrate, has obtained a methylpiperidine which differs slightly in its boiling point (107°) from that obtained by Cahours (b. p. 108), by the direct action of methyl iodide on piperidine.

Dimethylpiperyl iodide, $\text{N}(\text{C}_5\text{H}_{10})''\text{Me}_2\text{I}$, can best be obtained by heating piperidine with methyl iodide, and crystallising out from alcohol, in which the piperidine and methylpiperidine are readily soluble, but the dimethylpiperidine only moderately soluble. The base obtained from the hydriodide boils at $106\text{--}107^\circ$. When dimethylpiperyl hydrate is distilled, there is formed neither an alcohol nor a hydrocarbon, but a new base, NC_7H_{15} , thus:—



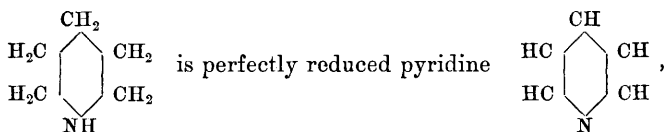
This base is a colourless liquid of a strongly ammoniacal odour (b. p. 118°). As the boiling point of this base agrees with that found by Cahours for the monomethyl compound, the author considers it probable that Cahours' specimen consisted to a large degree of the dimethyl base.

The author obtained a hydrochloride and an auerochloride, but was unable to obtain a crystalline platinochloride. In order to decide as to whether the dimethylpiperidine has the constitution $\text{C}_5\text{H}_9\text{Me}_2\text{N}$ or $(\text{C}_5\text{H}_9\text{Me})''\text{MeN}$, the author has studied the action of methyl iodide on this base, and has obtained *trimethylpiperyl iodide*, $(\text{C}_5\text{H}_9\text{Me})''\text{Me}_3\text{NI}$, which forms prismatic crystals (m. p. 200°). With moist silver oxide, the hydriodide forms the corresponding hydrate. When this latter is distilled, it is decomposed partly into dimethylpiperidine and methyl alcohol, and partly into piperylene, trimethylamine and water, thus:—



Piperylene is a liquid (b. p. 42°) which combines with bromine in excess, to form glistening crystalline leaflets (m. p. 14.5°) of a tetrabromide, $\text{C}_5\text{H}_8\text{Br}_4$. When dry hydrochloric acid is passed into dimethylpiperidine, a solid crystalline hydrochloride is first formed, which is subsequently decomposed at a higher temperature into methyl chloride and methylpiperidine. That this latter has the constitution— $\text{N}(\text{C}_5\text{H}_{10})''\text{Me}$, and not $\text{N}(\text{C}_5\text{H}_9\text{Me})''\text{H}$, is shown by the

fact that it combines with methyl iodide to form a compound, $N(C_5H_{10})''Me_2I$. This observation throws light on the constitution of the dimethylpiperidine: for if this base had the constitution $NMe_2(C_5H_9)$, it would be converted by the removal of one methyl-group into a secondary amine, $N(C_5H_9)MeH$; but if, on the other hand, it has the constitution $N(C_5H_9Me)''Me$, it will be converted by the removal of a methyl-group either into a secondary amine, $N(C_5H_9Me)''H$, or a tertiary amine, $N(C_5H_{10})''Me$. But the action of methyl iodide on the methylpiperidine shows that it is a tertiary amine: hence, in the formation of dimethylpiperidine the methyl-group enters into the group C_5H_{10} , from which it may again be removed by hydrochloric acid. Against König's view that piperidine—



the author considers that the removal of (trimethylated) ammonia from such a ring-constructed piperidine would leave a hydrocarbon of con-

stitution $\begin{array}{c} CH_2 \\ | \\ H_2C \text{ --- } \text{Cyclopentadiene ring} \text{ --- } CH_2 \\ | \\ HC \text{ --- } \text{Cyclopentadiene ring} \text{ --- } CH \end{array}$. Such a hydrocarbon would first take two bromine-atoms, and only by the loosening of the double affinity bond would take up four bromine-atoms. But piperylene combines most readily with bromine, which shows that the carbon-atoms are arranged not in a closed, but in an open chain. Piperylene differs from propyl- and isopropyl-acetylene by its behaviour towards ammoniacal solutions of silver and cuprous oxide; it is probably identical with Reboul's (*Ber.*, 14) valerylene, $CMe_2 : C : CH_2$.

The author proposes to study the constitution of piperylene more exactly.

V. H. V.

Supposed Identity of Paytine and Aspidospermine. By P. N. ARATA (Buenos Aires, Jan. 13, 1881).—Wulfberg having stated (p. 108 of this volume) that paytine, an alkaloid found in a white cinchona bark from Payta in Peru, is identical with aspidospermine from the bark of *Aspidosperma quebracho*, the author points out that the alkaloids obtained from these two sources differ somewhat in composition (the platinochloride of paytine containing 18.73 per cent. platinum, whereas that of aspidospermine contains only 17.45 per cent.), and vary considerably in some of their properties and reactions.

These differences are shown in the following table:—

<i>Paytine.</i>	<i>Aspidospermine.</i>
Easily soluble with 1 mol. H_2O .	White prismatic crystals, with brilliant faces.
Easily soluble in ether, benzene, chloroform, alcohol, and light petroleum.	Soluble in 48 parts alcohol, and in 106 parts ether; insoluble in light petroleum.

Paytine.

Slightly soluble in water.

Melts at 156°.

Heated above its melting point, it gives off an oily distillate, and leaves a carbonaceous residue.

Heated with caustic soda it yields a non-azotised sublimate, viz., paytone, which condenses in colourless laminæ and needles.

Dissolves in strong nitric acid, forming a liquid nearly colourless at first, but afterwards becoming garnet-red, and finally yellow.

Not coloured by ferric chloride or by strong sulphuric acid.

Mercuric chloride forms an amorphous yellow precipitate.

Auro-chloride: Purple precipitate, the supernatant liquid exhibiting the same colour.

The hydrochloride, hydrate, and nitrate of paytine are crystallisable; the sulphate, chromate, oxalate, and picrate, are not.

Aspidospermine.

One part dissolves in 6,000 parts water.

Melts at 205—206°.

Heated above its melting point, it decomposes partially, giving off an odour which resembles that of acrolein, and provokes sneezing.

Heated with an alkali, it exhibits the coloration of the pyridine and quinoline bases.

With nitric acid, it instantly produces a red-violet colour, which is persistent.

Sulphuric acid produces in solutions of aspidospermine a wine-red coloration, which disappears after some hours.

Precipitated by mercuric chloride in white tufts.

Deep blue coloration.

No crystallisable salts.

H. W.

Alkaloids of *Alstonia Constricta*. By O. HESSE (*Annalen*, 205, 360—371).—The name alstonine has been applied to several different substances by various chemists. The author proposes to restrict it to chlorogenine, prepared in the following way:—

The alcoholic extract of the bark is dissolved in water, saturated with hydrogen sodium carbonate, filtered, and the clear solution agitated with light petroleum to remove porphyrine and other bodies, the alstonine or chlorogenine, remaining dissolved in the mother-liquor, from which it may be extracted by saturating the solution with soda and shaking with chloroform; the black-brown chloroform solution is then treated with sufficient water and acetic acid, and the chloroform removed by distillation. The acid liquid, after filtration and treatment with animal charcoal, is precipitated by soda, when the impure brownish-yellow alkaloid is thrown down.

The purified alkaloid, $C_{21}H_{20}N_2O_4$, is a brown amorphous mass, which becomes darker in the desiccator, and finally coffee-brown, the change taking place rapidly at 80°. Freshly precipitated alstonine dissolves

readily in chloroform, but less readily when air-dried, easily in alcohol, but very sparingly in ether. Its hydrate (with $3\frac{1}{2}\text{H}_2\text{O}$) melts below 100° , whilst the dry alkaloid only becomes fluid at 195° (uncorr.).

Alstonine, contrary to Palm, is a strong base, and forms salts with the acids. A few were prepared and described earlier (1865). The platinumchloride has the composition $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4)_2\text{PtCl}_6\text{H}_2 + 4\text{H}_2\text{O}$. The sulphate, hydrochloride, tartrate, and oxalate are soluble in water, but an excess of these acids throws down the salts as brown flocculent precipitates. An acid constituent of the bark acts similarly to these acids, and forms a difficultly soluble compound with alstonine: the author considers it highly probable that this compound is Palm's alstonine.

Porphyryne.—Extracted with other bodies from the carbonate solution by light petroleum, from which acetic acid takes it up, with a splendid blue fluorescence, and gives a reddish-white flocculent precipitate with ammonia. This precipitate is dissolved in ether and treated with animal charcoal, which takes up not only a small quantity of the alstonine, but also another basic substance (*porphyrosine*), which can be dissolved out from the animal charcoal by dilute acetic acid with a splendid purple-red colour; the ethereal solution is then treated with dilute acetic acid, and the porphyryne precipitated by ammonia.

Porphyryne when purified forms a white amorphous substance (m. p. 97° uncorr.), readily soluble in ether, alcohol, and chloroform. A large excess of water added to the alcoholic solution produces a slight blue fluorescence. The alkaloid dissolves in concentrated sulphuric acid, with a purple colour; in sulphuric acid, containing chromic anhydride, a greenish-blue is produced, gradually becoming yellowish-green. Concentrated nitric acid dissolves it purple, soon becoming yellowish- or brownish-green. It gives a blue fluorescence in acid solution. Only 0.6 gram porphyryne were obtained from 2 kilo. alstonia-bark. Its composition is $\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_2$, and it forms a platinumchloride, $(\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_2)_2\text{PtCl}_6\text{H}_2$.

Alstonidine.—Separated from porphyryne by its less solubility in light petroleum, readily soluble in chloroform, ether, strong alcohol, and acetone, crystallising out on evaporation. Its solution in alcohol or in dilute acids has an intense blue fluorescence. Ammonia and soda precipitate it from its acid solutions in flocks, soon however becoming crystalline. It melts at 181° (uncorr.). It forms various salts, mostly crystallising easily. Its composition was not ascertained. It much resembles the alstonine of Oberlin and Schlagdenhauffen; but differs, as the latter is first turned bluish-green, then violet, and finally purpled, by sulphuric acid containing chromic anhydride.

The author considers that he has at present by no means exhausted the number of alkaloids in the bark of *Alstonia constricta*.

F. L. T.

A New Oxidation-product of Cholic Acid. By O. HAMMERSTEN (*Ber.*, 14, 71—76).—Crystallised cholic acid dissolved in glacial acetic acid, and treated with successive small portions of potassium dichromate likewise dissolved in acetic acid, is oxidised to

an acid of the formula $C_{26}H_{36}O_5$, which the author calls provisionally "dehydrocholic acid," from the fact that it contains 4 atoms of hydrogen less than cholic acid. The substance crystallises from its solution in hot water, in white microscopic needles, which are freely soluble in warm alcohol. Its solution in concentrated sulphuric acid is less highly fluorescent than that of cholic acid. The acid is monobasic, and forms easily crystallisable potassium, sodium, calcium, barium, copper, and lead salts. The methyl and ethyl salts are also crystalline. The acid does not exhibit the peculiar reaction of the bile-acids with Pettenkofer's test.

J. R.

Crystallisable Albumin from Pumpkin Seeds. By G. GRÜBLER (*J. pr. Chem.* [2], **23**, 97—137).—Pumpkin seeds are freed from the husk, reduced to powder, and elutriated with oil to separate the protein granules; these are then freed from oil by treatment with light petroleum and subsequently with ether, and extracted at the ordinary temperature with 10 per cent. sodium chloride solution, which dissolves the albumin and myosin. The latter is precipitated by neutralising the solution with ammonia, and the filtrate, on dilution with much water, gives a precipitate corresponding with Weyl's *vitellin*. This precipitate is again dissolved in a 20 per cent. sodium chloride solution, and the solution warmed and diluted until separation of the dissolved albuminoid begins to take place; on cooling gradually, microscopic octohedrons separate, which, after washing successively with water, alcohol, and ether, and drying over sulphuric acid, are obtained pure. They contain 5.31 per cent., and when air-dried about 10 per cent. of water. Crystals are also obtained from aqueous solutions of sodium acetate, nitrate, and phosphate; potassium bromide and iodide; ammonium chloride and oxalate, barium chloride, calcium chloride, magnesia sulphate, and potassium ferrocyanide.

The crystals obtained from sodium chloride solution contained 53.21 C, 7.22 H, 19.22 N, 1.07 S, 19.10 O, and ash 0.18 per cent.; and corresponding results were obtained by the analyses of the crystals furnished from the saline solutions.

Treated at 40° with magnesia and water, the albuminoid dissolves, and on cooling, microscopic crystals separate, containing 4.2 per cent. of ash, chiefly magnesia and phosphoric acid. A similar lime compound may be prepared.

O. H.

Crystalline Hæmoglobin. By G. HÜFNER (*Zeitschr. f. Physiol. Chem.*, **4**, 382).—There is great difference of opinion as to the existence of crystalline reduced hæmoglobin. The author kept blood in sealed tubes for one to two months, and at the end of that time found it crystallised, and argues that, after this long period, it could only be reduced hæmoglobin.

W. N.

Physiological Chemistry.

Formation of Glycogen in the Liver. By E. KÜLZ (*Pflüger's Archiv*, 24, 1—19).—Experiments made by the author on diabetic patients show that in cases in which the elimination of sugar by the urine has been reduced to a minimum, or caused to disappear by removal of all carbohydrates from the diet,—if a known quantity of white bread be given, the sugar elimination begins again in half an hour or thereabouts, attaining a maximum about the end of the second hour, and is over in from four to six hours from the time of taking the carbohydrates. These results are quite in accordance with those of v. Mering. The question arises, is the eliminated sugar the representative of the carbohydrates taken in, or is it possible for the conversion and elimination to take place so rapidly? The author quotes Seegen to the effect that this is improbable, but goes on to remark that Seegen offers no proof that such is not the case; whilst the experiments of Claude Bernard and Boussiguault support the theory; experiments by Windt, Kühne, Voit, Kölliker, Brücke, Hoppe-Seyler, and other authors are then quoted in evidence of the rapid formation both of bile and glycogen after food.

The details and method of 34 experiments are then given. Rabbits were the animals used; these were starved for six days, and then 25 c.c. of *syrupus simplex* was passed into the stomach by means of an elastic catheter; the animals were killed at gradually increasing times after the sugar was given, and the glycogen in the liver estimated by Brücke's method. The experiments show that four hours after the sugar was taken, nearly half a gram of glycogen might be found in the liver. The maximum was attained in 16—20 hours after; in all cases in which the experiment extended over 24 hours, no sugar was found in the stomach. A further series of experiments with grape-sugar, starch, milk, and grass are given with very much the same result. The author then comments upon Luchsinger's experiments upon dogs which had been starved for three weeks, and his conclusion, that either different parts of the liver contain different quantities of glycogen, or that the passage of blood containing sugar through the liver causes a formation of glycogen, and remarks that little value can be attached to them, since the experiment lasted only $1\frac{3}{4}$ hours; whilst, as the author has shown, four hours is required for the appearance of any very appreciable quantity of glycogen in the liver when sugar is introduced into the stomach, and seven experiments in which the sugar was injected into a vein are given, which strongly confirm this opinion. The urine was also examined and found to contain sugar up to the moment of death of the animal.

W. N.

Influence of Severe Bodily Exercise on the Amount of Glycogen in the Liver. By E. KÜLZ (*Pflüger's Archiv*, 24, 41—46).—Bernard's statement, "that in hybernating animals a large amount of glycogen accumulates in the liver, muscles, and lungs during the

period of hybernation, to be consumed when the animal awakens and begins to move, and that generally in mammals and birds (well nourished) when the muscles are at rest spontaneously, or are brought to rest by section of the nerves supplying them, glycogen accumulates in them to disappear on the resumption of activity;" and a list of investigators who have connected muscular activity with a consumption of glycogen are quoted by the author, who points out that we do not know whether the glycogen formed in rest is formed in the muscles, or brought to them from the liver by the blood.

Experiments were made upon five dogs, and the results are given in the following table:—

No. of Expt.	Body weight.	Food (daily).		Duration of exercise.	Weight of liver.	Glycogen of liver.
		Bread.	Meat.			
	grams.	grams.	grams.	hours.	grams.	
1	10,050	250	200	5½	255	trace
2	22,800	250	250	5	550	trace
3	11,720	250	300	5	240	0·8 gram
4	15,430	250	350	6	257	trace
5	39,520	500	1000	7	835	trace

This shows clearly that severe exercise will reduce the glycogen of the liver to practically nothing, and that five or six hours' exercise will produce a result which can otherwise be obtained only by starving the animal for from 12 to 20 days.

W. N.

Influence of Cold on the Amount of Glycogen in the Liver.

By E. KÜLZ (*Pflüger's Archiv*, 24, 46—48).—The author's experiments were performed on six rabbits in winter. In all cases these were immersed some time before death for one, two, or three minutes in ice and cold water. The livers, when examined in the usual way, were found in three cases to contain no glycogen, and in the remaining three only traces.

W. N.

Does Injection of Sodium Carbonate into the Portal Vein cause the Disappearance of Glycogen from the Liver? By E. KÜLZ (*Pflüger's Archiv*, 24, 48—52).—Pavy found this to be the case. The author deems it advisable to repeat the experiment with improved methods of estimating glycogen, since the possibility of error is very great. Pavy injected 200 grains of sodium carbonate in an ounce of water. The author used a 40 per cent. solution, which corresponds very closely. Four experiments were made on full-grown rabbits, without any special previous dietetic regimen; the solution was injected into a mesenteric vein.

No.	40 per cent. solution.	Duration of injection.	Animal lived after injection.	Glycogen of liver.
1	25 c.c.	15 min.	10 min.	1·3571 gram
2	22 „	10 „	20 „	0·5183 „
3	12 „	10 „	8 „	1·2510 „
4	25 „	11 „	5 „	0·3598 „
Small dog				
5	40 „	—	8 „	1·3520 „

For a sixth experiment a medium-sized old sheep-dog was used and fed for three days on bread, eating in all nearly 2 kilos. On the 4th day 40 c.c. of the same 40 per cent. solution was injected into a mesenteric vein, and half an hour afterwards the liver was found to contain 120 grams glycogen. From these experiments, the author concludes that Pavy's assertion is incorrect.

The results of several more experiments on rabbits are given, in which, although the dose of sodic carbonate was, considering the size of the animals, very large, it is very doubtful whether any effect at all was produced.

W. N.

Nature of the Sugar found in the Liver after Rigor Mortis.

By E. KÜLZ (*Pflüger's Archiv*, 24, 52—57).—The object of this paper is to show that although grape-sugar is found in the liver after death, there is good reason to believe that other allied products are present. Musculus and v. Mering assert that maltose is undoubtedly present; v. Limpricht has prepared large quantities of dextrin from horse's liver.

W. N.

Amount of Glycogen in the Liver and Muscles after Death.

By E. KÜLZ (*Pflüger's Archiv*, 24, 57—61).—The author states that he prepared glycogen from the liver of a patient (the subject of a very severe form of diabetes, and whose last meal (meat) was taken 34 hours before death), 12 hours after death. The case is interesting, as showing that glycogen is still formed in the liver in severe diabetes, and that it can be detected in the liver for a very considerable time after death. This led him to examine several livers for glycogen with the following results:—

88 gram liver of pig	3 days after death	1·2	gram glycogen.
191 „ „	8 „	0·910	„ „
275 „ „	5 „	3·45	„ „
57 „ ox liver	11 „	0·20	„ „
40 „ stillborn child	26 hours „	2·1053	„ „
58 „ dog	8 days „	4·20	„ „
(?) rabbit	3 „	1·579	„ „

The author then quotes Takác's statement that glycogen in the muscles diminishes very rapidly after death, and in one case disap-

peared entirely in 30 minutes, and gives the results of a series of experiments in this direction which go to show that this is by no means always the case, as glycogen was found in the muscles of one animal 26 hours after death. Nasse and Limpricht are quoted in support of the author's results. W. N.

Does Glycogen occur in the Blastoderm of the Chick? By E. KÜLZ (*Pflüger's Archiv*, **24**, 61—64).—From 116 embryos of 60 hours, the author obtained a substance (about 0.1 gram), which was apparently glycogen. Subsequent examination of the material of 5,000 fresh eggs gave a negative result. W. N.

Formation of Glycogen in Muscle. By E. KÜLZ (*Pflüger's Archiv*, **24**, 66—70).—From a series of experiments on frogs whose livers were removed, the author thinks it is probable that glycogen is formed by the muscular tissue. W. N.

Glycogen in the Livers of Hybernating Animals. By E. KÜLZ (*Pflüger's Archiv*, **24**, 74—80).—Schiff was the first to draw attention to this subject, and after him Valentin, Aeby, Luchsinger, Wolffberg, and Voit. The last-named investigated the glycogen of the liver and muscles of a marmot, and found them to contain 2.22 per cent. and 0.371 per cent. glycogen respectively, of which he remarks, since the animal had fasted for four months, and nothing tends to reduce the amount of glycogen in the organs so much as hunger, in this case the origin of the glycogen can only have been fat or albuminoids, and probably was formed during the period of hybernation. The author draws attention to the fact, that the total quantity found by Voit was not large, and quotes cases of dogs and rabbits whose livers contained as much as 100 grams of glycogen. He then quotes instances of considerable quantities of glycogen being found in the liver after 10 and 12 days' starvation. The results of experiments on four marmots were as follows:—

Time of killing.	Body weight at death.	
	grams.	Glycogen of liver.
1. 19/12/77	1100	0.3796 gram
2. 19/2/78	1071	0.3333 „
3. 4/1/78	3020	0.9909 „
4. 1 ¹ /3/78	2180	0.7545 „

The author is of opinion that although Voit may be right, it is more than probable that the glycogen formed in the liver after long hybernation may, after all, be but the residue of a large store laid in by the animal before winter; and in support of this theory, he quotes a case in which, after four months' hybernation, no glycogen could be detected in the liver. W. N.

Relation between the Molecular Properties of Inorganic Compounds and their Action on Living Animal Organisms. By J. BLAKE (*Ber.*, **14**, 394—398).—In isomorphous groups of metals, the physiological action of the members increases with their atomic weight. W. C. W.

Relation of the Number of Fish to the Lime present in Waters. By W. WEITH (*Bied. Centr.*, 1880, 914).—The investigation was undertaken at the instance of the Committee of the Berlin International Fishery Exhibition. Other conditions being similar, those waters were richest in fish which contained the most calcium bicarbonate dissolved, and the author showed by experiment that the carbonic anhydride given out by the fish dissolves the normal carbonate.

An important practical consequence of the research, if the views of the author are confirmed, would be not only that the fish would increase the dissolved lime, but that conversely the richness of the water in lime would increase its suitability for fish.

Aquatic plants on which fish subsist require carbonic acid, which is carried to them by the lime. J. F.

Quantity and Quality of Milk yielded by different Races of Cows. By W. FLEISCHMANN and P. VIETH (*Bied. Centr.*, 1881, 870—875).—These investigations were undertaken to ascertain the agricultural value of certain breeds of cows, chiefly of Mecklenburg stock; they are interesting only locally, containing nothing new either in feeding of the animals or in the manner of estimating the results.

J. F.

Composition of Human Milk. By J. FORSTER (*Ber.*, 14, 591—593).—M. A. Mendes has observed that the proportion of fat in human milk increases with each successive emptying of the mammary gland. Similar observations have formerly been made, not only with human, but also with asses' and cows' milk. In order to explain the phenomenon, Parmentier supposes a separation of cream in the sinus lactei, whilst Heynsius believes that the fat globules adhere to the fine lactiferous ducts, and are withdrawn by subsequent suction. The author has determined the solid constituents—fat, milk-sugar, ash and nitrogen—of samples of milk from nursing women, drawn from the breast about six hours after the last suckling of the child. He considers that Heynsius' hypothesis is plausible, but that further investigation is required to confirm it.

V. H. V.

Serum Albumin in Muscle. By B. DEMANT (*Zeitschr. f. Physiol. Chem.*, 4, 384).—The author compared the amount of serum albumin in the blood and muscles of two rabbits and a dog. The blood was defibrinated, then treated with a large quantity of 3 per cent. sodium chloride solution, decanted from the separated corpuscles, and magnesium sulphate added to the fluid to saturation, to precipitate the globulin. The muscles were treated in a similar manner, with the following results:—

	Serum Albumin per cent.	
	Blood.	Muscle.
Rabbit (1)	2.980	1.772
„ (2)	3.399	1.811
Dog	1.722	1.448

The quantity of serum albumin in the muscles suffers less variation

than that of the blood. The amount of blood in the muscles in the case of the rabbit was almost *nil*. In the dog the author estimated it at 6.06 per cent.

W. N.

Phenol Ethers in the Animal Body. By A. KOSSEL (*Zeitschr. f. Physiol. Chem.*, **4**, 296).—The author gave phenetol, $C_6H_5.OEt$, to dogs, in doses of from 8 c.c. to 10 c.c., and found subsequently in their urine a non-nitrogenous acid, of the formula $C_{14}H_{18}O_8$, "chinaethonic acid," which is levorotatory (about 63°), and does not reduce an alkaline solution of cupric oxide; it may be isolated by acidifying the evaporated urine strongly with sulphuric acid, and then shaking with ether. After distilling off the ether, the residue in the course of eight days yields warty masses of crystals, which may be obtained pure by recrystallisation from alcohol. Heated with acids, it decomposes into an acid, having apparently close resemblance to glycuronic acid, and an aromatic substance, which yields quinone on oxidation.

W. N.

Glycerolphosphoric Acid in Normal Human Urine. By SOTNISCHEWSKY (*Zeitschr. f. Physiol. Chem.*, **4**, 214).—Considering the wide distribution of lecithine and glycerolphosphoric acid in the tissues and fluids of the body, the author thought it would not improbably be found in the urine, and accordingly proceeded as follows:—10 litres of urine were treated with milk of lime and calcium chloride, to separate the phosphates; the filtrate was evaporated thoroughly, and the residue extracted with alcohol; the portion insoluble in alcohol was dissolved in water, and ammonia and magnesia mixture added, to get rid of phosphates still present. After standing for some time, this was filtered, and the filtrate boiled after strongly acidifying with dilute sulphuric acid. The fluid now contained free phosphoric acid, which could be detected by ammonia and magnesia mixture, and glycerol was detected by the acrolein and borax reactions, after evaporation and treatment with absolute alcohol.

W. N.

Occurrence and Origin of Methylamine and Methylcarbamide in Urine. By J. SCHIFFER (*Zeitschr. f. Physiol. Chem.*, **4**, 237).—The author has followed up the researches of Baumann and v. Mering on the subject, by boiling urine with strong alkalis. Dog's urine, after exclusive meat diet, was distilled with potash, and the ammonia received in hydrochloric acid. The evaporated residue gave Hoffmann's isonitril reaction, and also contained amine bases; these were also separated by treating the urine with milk of lime in the cold, and urine when so treated and boiled with potash yielded no amine bases.

Rabbit's urine gave the isonitril reaction only very feebly, or not at all. This the author attributes to the smaller quantity of creatine in the food of the Herbivora. The experiment of feeding a rabbit with creatine was tried, and the urine of the next 24 hours when distilled with potash gave a strong isonitril reaction, and also that of the next day. Creatine itself treated in this way gave no amine bases. The rabbit's urine, after feeding with creatine, yielded no amine bases to milk of lime: hence the author concludes that it could not contain any

methylamine, but only methylcarbamide. When the dog was put on a milk diet, the methylamine in the urine fell considerably. The conclusion is that the methylguanidine group of creatine is decomposed into ammonia, methylamine, and carbonic acid, but that only in rabbits the methylamine passes into methylcarbamide. When methylamine hydrochloride was given by the mouth, no methylamine was found in the urine of a rabbit until it was distilled with potash. W. N.

Oxidation of Aromatic Hydrocarbons in the Animal Organism. By M. NENCKI and P. GIACOSA (*Zeitschr. f. Physiol. Chem.*, **4**, 325).—After feeding with ethylbenzene, C_6H_5Et , hippuric acid was found in the urine of a dog; the ethyl group was also oxidised in the body; not more, however, than a sixth part of the quantity theoretically to be expected was obtained. The combined sulphuric acid of the urine showed no increase. Normal propylbenzene, C_6H_5Pr , was oxidised to benzoic acid; on the other hand, isopropylbenzene, $C_6H_5.CHMe_2$, yielded neither hippuric acid nor any aromatic acid. The combined sulphuric acid of the urine showed a decided increase, and apparently oxycymene was formed, although it was not isolated.

Butylbenzene was not oxidised to benzoic acid, although the sulphuric acid of the urine increased after it was given, and this increase extended over several days. By distillation of the urine with acids, colourless oily drops were obtained, probably hydroxybutylbenzene. Benzene produced much the same effect on the sulphuric acid as butylbenzene, only it lasted longer; phenol and catechol were found in the urine. After larger doses of benzene, quinol was also found in the urine (human).

Generally, the hydrocarbons were affected with difficulty; they remained a long time in the tissues, and the oxidation always affected the benzene nucleus itself, or the carbon-atom united with it. In men phenylglycollic acid in doses of 5 to 7 grams, appeared to have no influence on the fever temperature, and was eliminated unchanged.

W. N.

Chemistry of Vegetable Physiology and Agriculture.

Action of Ozone on Germs contained in the Air. By E. CHAPPUIS (*Bull. Soc. Chim.* [2], **35**, 380).--Dust collected from the air on plugs of cotton-wool, and introduced into solutions of yeast, caused a turbidity in a few days, but if the plugs containing the dust were previously subjected to the action of a current of ozonised air, no turbidity was produced at the end of 20 days. It is evident therefore that all germs suspended in the air, capable of developing in solutions of yeast from beer, are killed by ozone. C. H. B.

A Yeast Incapable of Producing an Invertive Fermentation. By E. ROUX (*Bull. Soc. Chim.* [2], **35**, 371—372).—A yeast was obtained

from a sample of altered glucose capable of producing fermentation in glucose, and which, like ordinary yeast, grows by budding, without forming mould, yet, unlike it, produces no fermentation in a solution of cane-sugar, notwithstanding its slow development, and that it derives from the sugar the hydrocarbons necessary for its growth. If the cane-sugar be inverted by the ferment of ordinary yeast or dilute acids, this yeast will produce rapid fermentation. It does not ferment milk-sugar. Like ordinary yeast, it will develop in yeast water free from sugar, and its cells present the same elongated and ramified appearance after living in the liquid after alcoholic fermentation has ceased.

L. T. O'S.

Influence of Heat on the Growth of Beets and Potatoes. By H. BRIEM (*Bied. Centr.*, 1880, 878—882).—There is no doubt that such atmospheric conditions as moisture, direction of air currents, pressure, &c., have great influence on vegetation, but they are only of secondary importance compared with that of heat, which is a primary factor.

The author commenced in March to plant beet seeds and potatoes at regular intervals, 1st and 16th of each month, noted the period of their first appearance above the ground, their period of full bloom and fitness for gathering, added together the temperature of each day, omitting all days colder than 4° C. (39·20° F.) in the case of beets, and 8° C. (50° F.) in the case of potatoes. The beets sown on 16th April and 16th June required a total temperature of 117° C. in each case, but in the former period it was spread over 12 days, with a daily average of 9·8°, and in the latter case equal progress was made in 6 days, with an average of 19·6°.

Potatoes afforded a still more striking example. On April 1st, the planting of one plot was made; it required 45 days to bring out the leafbuds; another plot planted on 16th June required but 14 days to reach the same stage, yet the total amount of heat received by both was the same—284—289° C°.; in one case, however, the daily average was only 6·4°, and in the other 20·3° C.

The same rule appears to hold good in every period of the growth of the experimental plants. The author puts it in the form of a law, that the higher the daily average of temperature, the more rapid the growth of the plant, but admits that the amount of moisture in the soil exercises considerable influence; and that heat without moisture is insufficient. He also admits that the requisite amount of heat spread over the whole period is far more efficacious than a low average followed by a sudden elevation of temperature. The author says as a result of his experiments, carried out carefully for two years, that too early planting of potatoes is injurious, but they should not be planted so late as to let their period of ripening run into the time when the daily average of temperature begins to decline.

J. F.

Fertilisation of Cereals. By V. LIEBENBERG (*Bied. Centr.*, 1880, 915—916).—A single bloom of wheat is shown to be capable of self-fertilisation, and a second experiment showed the possibility of externally effecting it, but apparently with less prospect of success; the probability is that self-impregnation is the rule, the other the excep-

tion. Rye-blossoms cannot successfully fertilise themselves. Rimpau from his researches concluded that single blossoms were not capable of self-fertilisation, but the author thinks that although such sterility may be a general rule, exceptions doubtless occur. Two ears of one and the same plant can fertilise each other; possibly the different results of the author's and Rimpau's researches are referable to different conditions of the flower.

With barley, according to Delphino, self-fructification is possible so long as the ear remains in its sheath. The author's experiments show that, as a general rule, cereals are self-fertilising, but are capable of impregnation from external sources. J. F.

Development of Sugar in Sorgho. By P. COLLIER (*Bied. Centr.*, 1880, 916).—In order to obtain the best results it is necessary to cut the stems while yet green, but fully ripe, that is, just when the seeds begin to harden and are nearly ready to fall; the plants at this time contain the largest quantities of saccharose and glucose, and the proportion between crystallisable and non-crystallisable sugar has reached its most favourable stage. The results are then most profitable. J. F.

Decomposition of Albumin in Plants. By E. SCHULZE (*Bied. Centr.*, 1880, 907—911).—This is a reply to a criticism on the author's previous papers. All albuminoids, when decomposed by acids or alkalis, have yielded aspartic acid, in addition to leucine, tyrosine, and glutamic acids, and no such compound has yet been examined which contains *one* of these amido-acids in overwhelming proportion with mere traces of the others; it is improbable that any albumin exists which is without leucine or asparagine-yielding atoms. These atom groups must necessarily be produced if albumin is formed in the plant at the cost of leucine, asparagine, or other nitrogenous organic material; in what manner this takes place is not understood, but it must be in consequence of, or accompanied by, radical alterations in their atomic combinations. When albumin decomposes in a plant, and in process of growth is reproduced, the asparagine is reabsorbed and albumin continues to be formed at the cost of the other amides; when the albumin is again decomposed, there is necessarily more asparagine present than originally existed. This accounts for the accumulation of asparagine in budding plants, and the author says that in previous communications he has not gone further than this, and repeats his theory that in consequence of repeated renewals and decompositions products of albumin are transformed into asparagine. J. F.

Investigation into the Cause of Beet-sickness in Soils. By J. KÜHN and others (*Bied. Centr.*, 1880, 859—865).—The symptoms of beet-sickness are very various, many of them being easily explained; others are difficult to account for; the latter are the subjects of the present investigations. Their general character is a falling off in the yield of roots and deterioration of their quality, occurring in strips and patches of the field; the disease quickly attacks the remainder of the crop, and renders whole districts useless for the cultivation of sugar-beets.

However reasonable the hypothesis may appear, that the disease is due to impoverishment of the soil by constant crops of the same root withdrawing the minerals necessary to the growth of beets, it is yet strange that the researches of Kühn on this subject, wherein he attributes the cause of the disease to the parasite called *nematod*, observed by Schacht, have not attracted more attention. The authors undertook to investigate the subject, and at starting proposed for solution the two following questions:—Firstly, has it been definitely proved, anywhere, that the sickness is due to deficiency of nutriment? and, secondly, have parasites appeared only in places where such a deficiency has been proved to exist, or are they found also in localities where there is abundance of the necessary plant food? To solve the first, analyses were made of healthy and sick soils. The nutritive constituents of the two were tolerably equal in amount, but the destructive parasites were numerous on the plants in the unhealthy portion in proportion to the intensity of the disease. As a further trial, chicory, a crop demanding the same materials for its growth as beet, was planted in one of the sick fields and it flourished greatly. The parasitic origin of the malady having been established, the problem of extirpating the parasite next presented itself, and was solved by burning the surface of the field after the manner recommended by Beatson. Fire was laid in trenches, and the surface soil lightly laid on the top; when ignited, further quantities were added in such a manner that a strong but dull heat is attained—a temperature of 50° killed but few of the insects; at 62° they were all killed; the field was re-tilled and re-sown with the best results, an excellent crop being obtained, and the fact demonstrated that the disease can be easily eradicated, and the same land used time after time for crops of beet—a most important matter to sugar manufacturers. The cost of burning is considerable, and could not be well applied on a large scale; but as a means of stopping the spread of the insects when they first appear, it is strongly recommended.

The authors carried out other interesting experiments by infecting healthy soil by means of the refuse of diseased roots, restoring them to their normal condition by burning and in other ways proving the truth of their discovery. Attempts to destroy the pest by chemical agents are discussed, but dismissed because of their great expense, caustic lime being the only material which can be recommended, and its efficacy is doubtful.

Experiments were afterwards made to ascertain if the nematods were peculiar to the beet, and for that purpose 180 different vegetables were planted in an infected field; very many of them were attacked, which weakens the theory of rotation of crops being a protection when burning is not resorted to. The authors recommend the fields to be thickly sown very early in the season; the roots when formed are attacked by the insect, and their larvæ can be removed by carefully pulling up all the young plants and destroying them; the field is then resown, and with a fair chance of better crops. Cautions are given against manuring with refuse of infected plants or dung of animals fed on such roots, and, in case of a rotation of crops, wheat or barley is recommended instead of oats or rye.

J. F.

Composition of Fodder. (*Landw. Versuchs.-Stat.*, 26, 318—321.)

—A commission on the motion of J. König has been appointed to consider the relative values of different kinds of fodder.

The following table of analyses has been formed by the Commissioners:—

	No. of analyses.	Average composition.					
		Water.	Protein.	Fat.	N-free extract.	Cellulose.	Ash.
Maize	46	14·21	9·86	4·54	66·85	2·91	1·63
Field beans.....	18	15·93	25·06	1·55	46·88	7·36	3·21
Lupines	12	13·50	35·56	5·15	27·23	14·56	4·00
Wheat bran (fine)....	21	12·07	14·05	4·17	58·34	7·30	4·07
„ (coarse) ..	89	13·57	13·56	3·37	54·98	8·85	5·65
Rice flour (fine).....	18	11·54	9·88	7·28	63·28	2·71	5·31
„ (coarse) ...	71	10·47	10·85	9·94	47·01	11·86	9·87
Rye bran.....	102	12·23	14·53	3·17	59·53	5·95	4·56
Rapeseed cake.....	133	11·24	31·11	9·89	29·18	11·19	7·39
Linseed cake.....	83	12·47	28·89	10·33	30·33	9·79	8·19
Poppyseed cake	11	11·54	32·74	7·84	23·46	12·15	11·27
Earthnut cake	35	11·15	46·12	6·64	25·82	5·64	4·63
Palmkernel cake	107	10·37	16·28	10·45	37·71	21·36	3·93
„ flour.....	45	10·92	17·13	3·70	41·34	22·99	3·92
Cocoanut cake	26	9·33	20·03	11·39	39·79	13·90	5·56
Sesame cake	27	12·14	36·77	12·00	20·31	8·47	10·31
Flesh-fodder flour....	19	10·60	72·66	12·27	0·72	—	3·75

J. T.

Cotton-seed Meal as Fodder for Milch Cows. By K. PRESSER (*Bied. Centr.*, 1880, 913—914).—The composition of the meal used in the experiments was:—

Water.	Protein matter.	Oil.	Non-nitrogenous extract.	Cellulose.	Ash.
11·3	31·6	9·6	29·4	11·0	7·1

The animals are described as somewhat unsuitable, but the results of adding the meal to their previous fodder was surprising; in every case there was a marked increase both in the flesh put on, and in daily yield of milk, the profit being greatly in excess of the additional cost of fodder.

J. F.

Examination of Linseed-cake and Meal. By F. HOLDENFLEISS (*Bied. Centr.*, 1880, 913).—Twenty-two samples were examined, and but ten found pure; as a rule the cakes were purer than the meals, not a single sample of the latter being free from adulteration. A favourite pretext for sophistication seems to be a desire on the part of the vendors to save the buyers trouble by breaking up the cake, the opportunity being taken to mix deleterious or worthless substances, which consist chiefly of mangold and rape-cake, wheat-chaff, clover-

cleanings, &c., &c. The pure cakes showed great variations in their composition, the oil ranging from 5·2 up to 17·5 per cent.

J. F.

Analysis of Forage Biscuits. By C. J. H. WARDEN (*Chem. News*, 42, 287).—These biscuits, obtained from Calcutta, were circular in shape, with a central hole, and weighed on an average 100 grams each. A physical examination resulted in the detection of linseed, peas, and husks not unlike those of barley. In order to obtain a sample for analysis, portions of several biscuits were pulverised. 100 pts. contained:—

Water.....	13·666
Albuminoids....	15·594 (= N × 6·33)
Carbohydrates ..	56·953
Fibre.....	1·237
Fat.....	7·623
Ash	4·927

The ash contained iron, phosphoric acid, sulphuric acid, and traces of nitric and carbonic acids, together with lime, &c. Chloride of sodium was present to the extent of 0·806 per cent. calculated on the biscuits. Fat is present in rather larger amount than is usual in the diet of horses. The linseed was probably in the form of meal after removal of most of the oil, and was most likely added as a material with which to agglutinate the other ingredients, and so admit of a finer biscuit being manufactured. It is at the same time nutritious, and forms fat. Nine horses were selected for experiment, all country bred, of nearly similar shape, size, and condition, and all subjected to the same treatment as regards work. They were watered three times a day before each feed; none of them had any bedding. The experiment lasted for about three months, and it was found that the nourishing properties of the biscuits were very good, and that, with one exception, all the horses had kept their condition and carried good coats. Three horses were fed on 4 seers of grain and about 15 seers of grass daily; three horses on 3 lbs. of biscuits and about 15 seers of grass; and three horses on 6 lbs. of biscuits only, no grass being allowed.

D. B.

Estimation of the Absorptive Power of Soils. By A. MAYER (*Bied. Centr.*, 1880, 912).—The author has devised an apparatus for the purpose of verifying the correctness of some theories previously enunciated in various agricultural publications. It consists of a zinc vessel made in the form of a prism, with a perforated bottom, 20 cm. high, and of 1 litre capacity. A sandy forest soil absorbed water equal to 26·3 per cent. in weight or 37·6 per cent. in volume when completely filled with the sample; 30·3 per cent. in weight and 42·4 per cent. in volume when the vessel was but half filled. A loamy clay from the drained part of Haarlem Sea absorbed, when filled, 42·9 per cent. weight, 44·1 per cent. volume, and, when half filled, 42·1 per cent. weight, 43·2 per cent. volume.

The author thinks that the estimation of the absorptive property

clay soils may be well carried out by older and hitherto rejected methods, but that there is a danger of inaccuracy with sandy soils.

J. F.

Removal of Iron from Newly-broken Soil. By C. PÄTZ (*Bied. Centr.*, 1880, 911—912).—Subsoil drainage is strongly recommended. The iron is generally found close beneath the surface soil, at the level of the subsoil water which carries it upwards, and it there forms with the sand present, hard reddish masses of almost stony nature, hard to work with the spade. The carrying out of an intelligent system of drainage, where the main drains are laid deeper than a meter, at right angles to the feeding drains, and at a distance between each two drains of ten times the depth, will prevent the rising of the water, and no iron will be found above the level of the pipes. The iron already present will be dissolved by rains and carried away.

J. F.

Continuous Cropping of Wheat and Barley. By A. VOELCKER (*Bied. Centr.*, 1880, 885—887).—This is a report of the third year of the continued growth of wheat and barley on certain light soils at Woburn. The results of both crops were less satisfactory than in preceding years, which is attributed chiefly to the very unfavourable character of the season, and, in the case of the wheat, to an attack of wire-worm and smut. The most unsuccessful plots were those unmanured, which were much behindhand both in grain and straw. Mineral manures applied to wheat and combined with ammonium salts yielded the best results. Mineral manures with sodium nitrate were less successful. Stable manure yielded a fairly satisfactory result. The author thinks that short, well-rotted stable manure is better for wheat than long and fresh.

The barley experiments do not differ materially from the wheat.

J. F.

Action of Water in the Process of Irrigation. By J. KÖNIG (*Bied. Centr.*, 1880, 849—855).—The beneficial effects of irrigation, according to Theil, are due to: 1st. The supply of indispensable water to the plant. 2nd. The prevention of heat by radiation. 3rd. The solution of plant-foods already present in the soil; and lastly, the direct supply of nutriment in the water itself. Vincent, as early as 1845, expressed the same opinion, but believed the oxygen and carbonic anhydride contained in the water had a certain effect. These theories induced the author of the present paper to undertake experiments which, continued over many years and on different meadows, have fully confirmed their truth.

The quantity of water originally used was measured, as was also that flowing away, certain errors being unavoidable from the variations of temperature and from the liability of the water to leak away into the subsoil through holes or soft places.

The quantity of inorganic matter abstracted from water in flowing over a meadow varies according to the season, being greater in summer than in winter. It corresponds with the more or less vigorous growth of the plants, and does not arise from absorption by the soil (potash, ammonia, and phosphoric anhydride excepted). The poverty or rich-

ness of the soil in certain ingredients affects the results. An example is given of the summer irrigation of a certain meadow:—

	CO ₂ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	SO ₃ .	NO ₃ .
Unused water. .	208.4	121.0	5.4	1.9	4.3	16.3	2.3
Water used frequently. }	228.9	132.7	6.3	1.5	3.8	14.7	1.6

Calcium and magnesium have been withdrawn from the soil in proportion to the increase of carbonic acid on the used water.

The winter irrigation shows an increase of sodium, sulphuric acid, and nitric acid, the reverse of that in summer.

Suspended matters invariably sink to the bottom; therefore, water can be employed as a vehicle for manures with very good effect. As an example the author gives the following:—From a certain meadow, in which a course of daily irrigation was carried out, a crop of 4,000 kilos. of hay per hectare was taken. The quantities removed from and added were as follows:—

	K ₂ O.	Na ₂ O.	CaO.	MgO.	P ₂ O ₅ .	SO ₃ .
4000 kilos. hay re- moved }	52.8	10.4	34.4	13.2	16.4	9.6
Added during irri- gation }	6.1	75.7	69.8	26.6	3.2	54.8

The water of rivers and streams contains more or less materials required by plants; but in clear waters, which do not flow through populous places, the phosphoric acid is in very small quantity. The author's experience leads him to recommend manuring with superphosphate in combination with irrigation.

Irrigation water does not always have a manurial effect, but its beneficial action is due to the oxygen it contains stimulating and facilitating other chemical combinations. However, the author has not been successful in estimating the increase or decrease of oxygen. He attaches considerable value to irrigation as a regulator of the temperature of the soil; the latter is a better conductor of heat than water. In cold seasons, water being warmer than the earth, the heat is quickly absorbed. In autumn the irrigated land is protected by the water from the early frosts. In spring, the warmer irrigation water helps to thaw the hardly-frozen soil and allows vegetation to start. From this cause irrigated meadows are at this season greener and fresher in appearance than other meadows not so treated. In summer the case is different; the water is then colder than the soil, and it cools the heated fields. Sewage added to the water used for irrigation yields up all its valuable ingredients to the soil, and when several times employed, it is found to retain no traces of its manurial qualities.

J. F.

Rotation of Crops. By A. VOELCKER (*Bied. Centr.*, 1880, 887—890).—The third annual report of a four-yearly rotation of crops on the experimental farm at Woburn. The first parcel was sugar-beet following wheat; there were four divisions differently manured, but the results of all were inferior to the preceding year, owing, in the

author's opinion, to the unfavourable weather, deficiency of heat and sunshine, &c. The second division was a clover and rye-grass mixture, following barley. Sheep were let in on the stubble and fed with artificial food, the time they were on the field varying on each plot; the crop was also inferior to the previous year. Wheat succeeding rye-grass, and barley following sugar-beets were the other crops, and they turned out well, considering the bad season and the light nature of the soil at Woburn; their yield was larger than in the previous year.

J. F.

Manure. By FLEISCHER (*Landw. Versuchs.-Stat.*, **26**, 385—388).—The author has communicated analyses of the nightsoil of the towns of Groningen, Emden, and Bremen.

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
H ₂ O	61·4	97·1	31·7	18·5	55·7	27·8
Insol. in HCl ..	17·4	—	35·6	—	—	—
N	0·6	0·29	0·52	0·22	0·43	0·79
K ₂ O	0·24	0·36	0·26	0·22	0·42	0·66
CaO	1·8	—	2·71	—	1·77	2·43
P ₂ O ₅	0·5	0·07	0·51	0·31	0·48	0·95
Total solids	—	2·9	—	—	—	—

(1) Is the mean of four analyses of Groningen compost; (2) is the mean of two analyses of liquid manure collected in the same town; (3) is the mean of three analyses of pail manure from the town of Bremen; (4) street-sweepings from Bremen, mean of three analyses (the constituents suitable for plant-food only given); (5) Emden compost, new; (6) Emden compost, old.

J. T.

Comparative Value of Soluble and Insoluble Phosphates.

By A. VOELCKER (*Bied. Centr.*, 1880, 866—867).—This paper is a summary of conclusions arrived at by the author after a controversy which had its origin in field trials made by Jamieson in Scotland, from which he argued that crude phosphatic materials, finely pulverised, were very nearly as valuable as superphosphates for the growth of Swedish turnips. Voelcker views the matter from another standpoint, and after quoting numerous experiments made by himself and others, enunciates his opinions in the following eight propositions:—

1. Phosphates are not readily taken up by plants in a soluble form, but must be returned to an insoluble condition before they yield their useful properties.

2. The efficacy of insoluble calcium phosphate corresponds with the minuteness of division in which it is found in a manure.

3. The finer the particles in a phosphatic material, the easier it is dissolved in water, and the more energetic its action as a manure. Coarsely-ground coprolites and other minerals are less useful than the same materials in fine powder.

4. Calcium phosphate, in porous soft bones, is more soluble and energetic than in hard bones, and is more available in bone meal than in crushed bones.

5. Calcium phosphate, in crystallised mineral phosphates, Norwegian,

Canadian, and Spanish apatites, for example, is less soluble and energetic than the same amount contained in porous phosphatic materials, such as certain descriptions of phospho-guano.

6. Treatment with acids renders the material completely soluble in water, and the so-formed superphosphate, when put into the ground, is precipitated in a very fine state of division.

7. In this precipitated state, the insoluble phosphate is immeasurably more finely divided than it could be obtained by mechanical means, and is consequently more energetic than any raw material mechanically ground.

8. The author's conclusion is, that the chemical treatment with acid is the cheapest and best way of rendering mineral phosphates useful for agricultural purposes. J. F.

Experiments with Artificial Manures. By P. GENAT (*Bied. Centr.*, 1880, 867—868).—At the instance of the Agricultural Union of Lunéville, the author carried out an extended series of experiments with artificial manures applied to different soils and plants. With rye, the manuring showed a certain increase, but only in the case of peanut-cake was there a decidedly profitable return.

Oats showed beneficial results with all kinds of manure, especially nitrogen, on poor soils, but on rich soils the increased production was inconsiderable.

Meadow, in two series of experiments, did not yield sufficient surplus crop to cover the cost of the manure.

Potatoes were also tried in two series, in soil which was previously in good manurial condition. One result showed a deficiency; the other a slight increase. In an additional experiment with very dry soil, the crop was very good, and the price of the article being high, a fair profit was made.

In all cases results were compared with those on unmanured plots.

J. F.

Composition of Two Samples of Peat. By A. PETERMANN (*Bied. Centr.*, 1880, 912).—Both samples were air-dried :—

	No. 1.	No. 2.
Water at 100° C.	19·02	29·37
Organic matter.....	77·09	55·37
Ferric oxide	0·39	1·11
Potash	0·07	0·22
Soda	0·23	0·46
Lime	0·25	3·96
Magnesia	traces	0·35
P ₂ O ₅ —Cl—Fe ₂ P ₂ O ₈	traces	traces
Sulphuric anhydride ..	0·26	1·33
Sand and silicic acid ..	2·69	7·33

100·00

100·00

Containing nitrogen.... 0·99 p. c.

0·62 p. c.

J. F.

Potatoes Manured with Peat, Nitrophosphate, and Sodium Nitrate. By W. H. (*Bied. Centr.*, 1880, 868—870).—The experiments were made with the common American fodder potato, in an elevated field with clean sandy soil, previously well tilled and cropped with lupines, winter rye, and American potatoes.

The manures employed were, in five experiments, equal amounts of peat soil, to two of which different quantities of ammonium phosphate, and in three, of sodium nitrate, were added; the sixth plot was strongly manured with peat alone, the seventh with good stable manure, and the eighth with nine two-horse wagon-loads of compost, saturated with dirty water, and layered with pond slime, &c. The result of the nitrogen in the Chili saltpetre far exceeded that of the phosphate in the nitrophosphate. Very startling was the effect of the peat alone, which yielded better results than even the stable manure; it was probably obtained from a low-lying moor, rich in nitrogenous matter. In the comparison, it should be noted that no information is given as to the quantities of phosphoric acid and nitrogen contained in the manure employed in the first five experiments. J. F.

Analytical Chemistry.

A Simple Method of Determining Boiling Points. By B. PAWLEWSKI (*Ber.*, **14**, 88).—The apparatus employed consists of a flask of 100 c.c. capacity, half-filled with glycerol (or with sulphuric acid, aniline, or paraffin), into which dips a test-tube of thin glass, 15–20 cm. long and 6–7 mm. wide, passing through a cork in the mouth of the flask. A few drops (·5–1·5 c.c.) of the liquid under examination are introduced into the tube, and a thermometer is held above the liquid by a stopper in the mouth of the tube. A small side opening in the tube, just below the stopper, allows the escape of vapour. On heating the contents of the flask, the thermometer rises rapidly up to the boiling point of the liquid in the tube, and then remains stationary until the whole of the liquid is evaporated, notwithstanding that the temperature of the bath may rise much higher. The method is said to be rapid, easy, and exact. J. R.

Action of Organic Acids on Minerals. By H. C. BOLTON (*Chem. News*, **43**, 31–34).—The author has investigated the action of citric acid, alone or mixed with certain salts, on 105 minerals, a list of which is given, classified in the groups (1) sulphides, arsenides, tellurides, &c., (2) oxides, (3) silicates, (4) miscellaneous. The reagents used were (1), “citric acid,” an aqueous solution of the acid saturated at 18–23°, (2) “nitro-citric mixture,” solution (1) with addition of solid sodium or potassium nitrate (3) “iodo-citric mixture,” solution (1) with addition of solid potassium iodide at the time of testing.

Sulphides, arsenides, &c.—Clausthalite and leucopyrite dissolve in

cold citric acid without evolution of gas. Alabandite is strongly attacked in the cold, with evolution of hydrogen sulphide, and is completely dissolved on heating. It appears to be the most easily decomposed of all the 37 sulphides yet examined. Boulangerite, jamesonite, and kermesite are more or less attacked by the boiling acid, but the remaining minerals of the first group, and sulphur, resist its action. All the twenty-five minerals of the first group, with the exception of realgar, orpiment, and proustite are rapidly and completely dissolved by the "nitro-citric mixture," in some cases with production of solutions of characteristic colour, and even sulphur is partially oxidised to sulphuric acid. Realgar and orpiment are partially decomposed by boiling with the "iodo-citric mixture," but proustite and sulphur resist even prolonged heating. All the other members of group (1) are readily dissolved by it. These reactions afford further proof of the differentiating power of these reagents.

Oxides.—Corundum, spinel, chrysoberyl, cassiterite, rutile, hyalite, and quartz, resist the action of all three reagents. Gummite is attacked by cold citric acid, and melaconite and goethite are partially soluble on heating. Menaccanite and washingtonite are slightly attacked by nitro-citric mixture, and strongly by iodo-citric mixture, which also attacks braunite and goethite.

Silicates.—Cold citric acid decomposes willemite, pectolite, calamine, natrolite, wollastonite, chrysolite, chondrodite, chrysocolla, apophyllite, rhodonite, analcite, chabazite, stilbite, deweylite, nephelite, lapis lazuli, laumonite, herschelite, thomsonite, mesolite, and prochlorite. In the first four and some other cases with gelatinisation. The boiling acid strongly attacks tephroite, ilvaite, giesseckite, jefferisite, heulandite, genthite, datolite, prehnite, normal serpentine, chrysotile, and retinalite, but has little action on parasite, pyrope, almandite, colophonite, phlogopite, bastite, masonite, bowenite, and probably allanite. On the whole, citric acid acts on the silicates with the same energy as hydrochloric acid. The nitro-citric mixture is not more powerful in its action than citric acid alone, but the iodo-citric mixture attacks the garnets already mentioned, besides enstatite, hypersthene, pargasite, epidote, olivine, augite, and almandite. On the other hand, orthoclase, albite, labradorite, hornblende, spodumene, pectalite, actinolite, asbestos, beryl, zircon, vesuvianite, zoisite, iolite, lepidolite, leucite, and alusite, fibrolite, topaz, titanite, staurolite, kaolin, wernerite, diopside, kyanite, talc, muscovite, biotite, ripidolite, and tourmaline, are not attacked at all, or give up only a trace of iron. C. H. B.

Quantitative Estimation of Chlorides in Urine. By DAL-KOWSKI (*Centralblatt f. die med. Wiss.*, 1881, 177—178).—The author has for some time used Volhard's method of direct estimation with silver and ammonium thiocyanide, which is conducted as follows:—10 c.c. of urine are put into a 100 c.c. flask, and diluted to about 60 c.c. 2 c.c. HNO_3 (sp. gr. 1.2) and 15 c.c. silver solution (1 c.c. = .01 NaCl) are then added, the mixture is well shaken, the flask being kept closed; distilled water is then added up to the mark, and the whole filtered; the filtration takes but a short time, and the filtrate is absolutely clear. 80 c.c. of the filtrate are placed in a 250 c.c. flask,

with 5 c.c. of a solution of ammonio-ferric sulphate (saturated in the cold, and free from chlorides), and the quantity of silver estimated by ammonium thiocyanide solution; the end of the reaction is determined by the blood-red colour of the ferric thiocyanide produced, and is exceedingly sharp—the thiocyanide solution being titrated with the silver solution used—by this method four estimations can easily be made in an hour. The calculation is simple, and the results obtained from several operations on the same urine exceedingly concordant. The author then points out the well-known defects of the methods of titration with silver using potassic chromate as an indicator, and titration in the ash, after fusion with soda and potassic nitrate, and recommends the use of the method above described. W. N.

Detection of Iodine in Urine. By F. FIELD (*Chem. News*, **43**, 109).—Although a solution of iodide is a very sensitive test for platinum, the converse does not hold good. The employment of a platinum salt for the detection of iodine is therefore useless. Urine known to contain iodine in the form of a potassium salt gave no coloration whatever with chloride of platinum, although, on addition of starch-water, a blue colour was speedily developed when the iodine was liberated, and a drop of chloroform was coloured pink when added to the liquid. Experiments in this direction led the author to the investigation of the detection of iodine in urine. Giannetti states that urea destroys the colour of iodide of starch, but that urine destroys the colour of this compound more quickly than it would be destroyed by the corresponding quantity of pure urea in aqueous solution. The author's observations fully confirm this, and he supposes that it is not the urea, but some other organic matter in the urine to which this reaction is due. His results indicate that neither the platinum nor palladium test can be used with any certainty for the detection of iodine in urine; that the reaction of free iodine on starch-water is even more delicate than the same element on bisulphide of carbon, benzene, or chloroform; and that in order to prove with certainty the existence of iodine in the excretion, it is necessary to destroy the organic matter before applying the test. D. B.

Laboratory Observations. By F. FIELD (*Chem. News*, **43**, 180—181).—The rose-colour produced by a solution of platinum chloride in potassium iodide is destroyed by urine, albumin, tannin, gallic acid, pyrogallol, potassium cyanide and thiocyanate, and the liquids in which meat or vegetables have been boiled. No alteration in colour is produced by starch, cane or grape sugar, gum, dextrin, gelatin, glycerol, nitrous and oxalic acids. Although the destruction of the colour by any water, would not prove the presence of any of the former substances, still the fact of the colour not being destroyed would show their absence and prove the water to be comparatively free from sewage contamination. L. T. O'S.

Estimation of Small Quantities of Phosphoric Acid. By KÖNIG (*Landw. Versuchs.-Stat.*, **26**, 360—364).—In a paper on the azotometer, Dietrich remarks, that in precipitating phosphoric acid with

ammonium molybdate, the proportion between the phosphoric acid and the ammonium in the precipitate is constant. König has tried to found a method for estimating small quantities of phosphoric acid on this constant ratio. Up to 5 mgrms. of acid the results are tolerably accurate; with 7 mgrms. the results vary as much as 0.5 mgrm.

J. T.

Insoluble Phosphate Estimation. By FLEISCHER (*Landw. Versuchs.-Stat.*, **26**, 355—358).—The author unfavourably criticises the method of estimating phosphoric acid by extracting insoluble phosphates with ammonium citrate.

J. T.

Grains of Silica and Micrococci in the Atmosphere. By T. L. PHIPSON (*Chem. News*, **43**, 28).—In addition to angular fragments of mineral matter, the dust of the atmosphere contains a number of very minute, more or less transparent, spherical bodies, very similar in size and shape, which resist the action of hydrochloric acid, and of a white heat. Siliceous algæ lose their forms when subjected to even a moderate temperature; fossil diatoms, on the other hand, resist the action of heat and of acids. It is probable, therefore, that the siliceous bodies present in atmospheric dust are really fossil micrococci.

C. H. B.

Decomposition of Slags and Silicates. By M. W. ILES (*Chem. News*, **43**, 78).—From 45 to 50 grams pure potash are fused in a large silver crucible, until the mass has assumed a quiet fusion. 1 gram finely-powdered silicate is introduced upon the surface of the cooled mass, and the heat is gently applied, increasing it toward the end of the fusion. Manganate, silicate, and aluminate of potassium will be formed, and the iron will remain as sesquioxide; however, compared with the ordinary mode of fusion with alkaline carbonates, there is a marked difference in the time required for the performance of the process, and the rapidity of the disintegration of the fused mass when treated with water. The lead (if present) will not attack the silver crucible in the slightest degree; it must be remembered, however, that fused potash or soda will slightly attack silver vessels, and it is necessary to take the precaution of washing the silicic acid with some solvent for argentic chloride.

This method suggests a mode of separating aluminium from iron, also a volumetric method for the determination of manganese, since potassium manganate is quite stable in presence of excess of alkali.

D. B.

Determination of Sulphur in Sulphides, and in Coal and Coke. By T. M. DROWN (*Chem. News*, **43**, 89).—Most of the simple sulphides, as blende, pyrites, &c., when exposed to the combined action of an alkaline hydrate and bromine, and finally to hydrochloric acid, are completely and promptly dissolved. The process usually adopted is advantageously simplified, by making a saturated solution of bromine in the concentrated alkali. This is done by pouring bromine into a soda solution of sp. gr. 1.25, until no more is taken up, and then adding a little more soda solution until the liquid no longer gives off free bromine. This method of determining the sulphur was found especially useful in the analysis of coal.

The author has in progress an interesting investigation on the effect of coking on the sulphur in coal, to determine what influence the nature of the sulphur—whether in combination with iron as pyrites, or originally combined with the coal—has on its elimination in coking.

D. B.

Characteristic Colour Reactions with Sulphydrates. By P. CLAESSON (*Ber.*, **14**, 411—412).—Sulphydrates exhibit a characteristic coloration when a few drops of dilute ferric chloride are added to their aqueous alcoholic solutions, which have been previously mixed with ammonia. Under these conditions methyl, ethyl, amyl, benzene, and toluene sulphydrates, toluene disulphydrates, and thiocetic acid yield a dark reddish-brown coloration; thiolactic and thioglycollic acids give a dark reddish-violet; metallic thiocyanates and thiosulphates produce a dark red, and sulphydrates of the metals of the potassium and calcium groups form a green coloration.

W. C. W.

Estimation of Phosphorus in Steel. By J. O. ARNOLD (*Chem. News*, **43**, 147—148).—The author, after showing the inaccuracy of the results obtained by estimating the phosphorus in steel directly as pyrophosphate of magnesium, or ammonium phosphomolybdate, applies the ordinary indirect method with molybdic acid and magnesium mixture as follows. The steel is dissolved in nitric acid (sp. gr. 1.20), and the iron reduced with sodium sulphite; after expelling the sulphurous anhydride, the phosphorus is precipitated as basic phosphate and acetate. The precipitate is dissolved in hydrochloric acid, evaporated to a small bulk, ammonia added, and the precipitate formed is dissolved in nitric acid (sp. gr. 1.40). Ammonium molybdate is added in excess, and the solution boiled, the precipitate is collected, dissolved in ammonia, and the phosphorus estimated as magnesium pyrophosphate.

L. T. O'S.

Estimation of Chromium in Iron and Steel. By J. O. ARNOLD (*Chem. News*, **42**, 285).—Weigh out from 1 to 5 grams of the steel (in drillings), according to the amount of chromium present. Place the metal in a wide covered beaker, and add 20 c.c. of strong hydrochloric acid, heat until all action is at an end, and evaporate gently to complete dryness; thus the chlorides may be almost entirely detached from the bottom of the beaker in a brittle cake, which is broken up into small pieces, and as much as possible is brushed out into a clean dry porcelain dish. A small quantity of chloride will, however, remain adhering to the beaker, this may be removed with 2 or 3 c.c. of dilute hydrochloric acid, the solution being transferred to a platinum dish and evaporated. When dry the main quantity of the chlorides is carefully brushed out of the porcelain dish into the platinum dish, and mixed with an excess of fusion mixture (1 part Na_2CO_3 and 1 part KNO_3). It is then transferred to a crucible, and fused with the cover on until quite liquid. This converts the iron into insoluble oxide; the manganese, silicon, and chromium into alkaline manganate, silicate, and chromate. The fused mass is dissolved in 80 c.c. boiling water, 3 or 4 drops of alcohol are added to decompose

the manganate, and the oxides of iron and manganese allowed to settle thoroughly. When clear, the supernatant liquid is decanted on a close double filter, the latter is washed with hot water, and the precipitate washed twice by decantation with 30 c.c. hot water. As the oxide of iron is in an exceedingly fine state of division, these precautions must be adhered to, otherwise some of it may pass through into the filtrate. The latter contains the chromium and silicon, and is treated with 20 c.c. of hydrochloric acid, the solution being well boiled, with the usual precautions, to expel all carbonic acid and nitrous fumes. Dilute ammonia is next added, and the solution heated nearly to boiling; the precipitate, consisting of $\text{Cr}_2(\text{HO})_6$ and $\text{Si}(\text{HO})_4$, mixed with alkaline salts, is collected on a filter and slightly washed. It is then dissolved off the filter with hot dilute hydrochloric acid, and received into the beaker in which the precipitation took place. The solution is evaporated to convert the $\text{Si}(\text{HO})_4$ into SiO_2 . The soluble chloride of chromium is taken up with 10 c.c. of hydrochloric acid and 90 c.c. of water, and is filtered through a washed filter into a beaker. The precipitation is now repeated as above, and the $\text{Cr}_2(\text{HO})_6$ comes down free from silica and alkaline salts. It is collected, washed, dried, ignited, and weighed as Cr_2O_3 .

The author mentions that with average care the error will never exceed 0.05 per cent. A duplicate estimation can be carried out in a day and a half.

D. B.

Estimation of Silicon and Titanium in Pig-iron and Steel.

By T. N. DROWN and P. W. SHIMER (*Chem. News*, **42**, 299—302).—The estimation of silicon in iron and steel by dissolving the metal in hydrochloric acid does not give good results, partly because a certain proportion of the silica, depending on the strength of the acid employed, remains in solution, and partly because the silica is often mixed with titanitic acid. The following method has been found uniformly accurate and trustworthy. Treat the iron with nitric acid until all action ceases; then evaporate with sulphuric acid until the nitric acid is expelled; filter; wash the siliceous and carbonaceous residue with hydrochloric acid and hot water; then ignite and weigh the silica, which is pure and free from titanitic acid. The iron may also be carefully fused with 25 times its weight of potassium hydrogen sulphate; the fused mass is then treated with water, with addition of a little hydrochloric acid to dissolve the ferric oxide adhering to the crucible, and the silica filtered off. This method does not, however, give uniformly accurate results, especially with iron and steel containing but little silicon.

To estimate titanium in pig-iron, the metal may be heated to redness in a porcelain boat in a current of dry chlorine. The ferric chloride formed is condensed in the cool part of the glass tube in which the boat is heated, whilst the more volatile silicon and titanium chlorides are collected in a series of three or four wash-bottles containing water. The contents of the wash-bottles are evaporated with about 15 c.c. of sulphuric acid (sp. gr. 1.23) until all hydrochloric acid is expelled. The silica is thus rendered insoluble, and may be filtered off: the titanitic acid remains in solution, and may be precipitated by boiling, after dilution with water. This process gives somewhat higher results

than Riley's method, and is more accurate; it cannot however be employed for the estimation of silicon, since the amount of silicon obtained is always too low. The ferric chloride formed always contains traces of manganese and phosphorus, and the water in the wash-bottles contains sulphur in the form of sulphuric acid. The residue in the boat contains—in addition to the manganese—aluminium, magnesium, and calcium, which may have been in combination with the iron, or may have been derived from admixed slags. When blast furnace slag is mixed with charcoal, and heated in a current of chlorine, no silicon chloride is formed.

Numerous analyses of iron and steel are given showing the accuracy of the processes. C. H. B.

Determination of Basic Cinder and Oxides in Manufactured Iron. By W. BETTEL (*Chem. News*, 42, 100).—5 grams of the borings are heated with a solution of 10 c.c. bromine, and 35 grams potassium bromide in 150 c.c. water. Heating is continued until the iron is dissolved; and the solution is filtered, drained, and washed with a solution of sulphurous acid containing 5 per cent. of hydrochloric acid. When the filtrate is practically free from iron, wash with boiling water containing 0.5 per cent. hydrochloric acid, then with pure water, rinse into a small platinum dish, evaporate to a small bulk, and dissolve out silica by means of a hot solution of sodium carbonate. Boil, dilute, filter, wash with hot water, then with a 0.5 per cent. solution of hydrochloric acid, finally with water, dry, ignite, and weigh. Determine the silica in the residue in the ordinary manner. To those who object to the bromine process, the author would recommend the following method: 5 grams of the finely-divided iron are dissolved in 60 c.c. clear solution of cuprous chloride (1 in 2), mixed with 100 c.c. saturated solution of potassium chloride, and 50 c.c. of dilute hydrochloric (1 in 20), are added. When no particles of iron can be felt by the aid of a glass rod, the mixture is boiled, filtered, and the residue washed with potassium chloride solution until all the copper is removed; then with hot dilute hydrochloric acid (1 in 50), finally with hot water. Separate the silica as before. If the copper obstinately adheres to the paper, slip over the tube of the funnel a piece of india-rubber tubing with clip, fill up funnel with strong liquid ammonia, cover, and leave the whole at rest for half an hour, then proceed with dilute acid, &c., as before. The results of both processes are said to agree with Fresenius's method. D. B.

Detection and Estimation of Arsenic in Organic Matter. By R. H. CHITTENDEN and H. H. DONALDSON (*Chem. News*, 43, 21—24).—1. *Method for the Complete Extraction of Arsenic from Organic Matter.*—Gautier's method of destroying the organic matter is based upon the older methods of Orfila and Filhol, consisting of successive oxidations with nitric acid and sulphuric acid at elevated temperatures. The first part of the authors' process is practically the same, except that they use a much lower temperature. After oxidation, the arsenic exists as arsenic acid readily soluble in water. This is extracted from the carbonaceous matter by repeated treatment with boiling water.

The reddish-brown fluid containing some organic matter and arsenic is then evaporated to dryness with the usual precautions, and the residue dissolved in a definite quantity of a dilute solution of sulphuric acid, introduced into the Marsh apparatus, and the arsenic weighed in the metallic state in the manner about to be described.

2. *Marsh Apparatus*.—The Marsh apparatus is modified in the following manner:—The flask, a Bunsen's wash-bottle of 200 c.c. capacity, is provided with a small separating funnel of 65 c.c. capacity, with a glass stop-cock. In this manner a slow and even evolution of gas is obtained by arranging the funnel filled with the acid mixture so as to give a constant and regular supply of fluid at the rate of two or three drops per minute. The gas generated is passed through a calcium chloride tube and then through a tube of hard glass, heated to redness by a miniature furnace of three Bunsen lamps with spread burners, so that six inches of the tube is uniformly heated: with a proper length of cooled tube not a trace of arsenic passes by. The glass tube, when the quantity of arsenic is very small, is so placed that the mirror is deposited in the narrow portion; but when the arsenic is present to the extent of 0.005 gram, the tube should be 6 mm. in inner diameter, and so arranged that fully two inches are between the flame and the narrow portion. The arsenic being collected as a large or small mirror of metal, the tube is cut at a safe distance from the mirror, so that a tube, of say 2—6 grams weight, is obtained. This is carefully weighed, and the arsenic removed, either by simple heating or, if it is to be saved as in a toxical case, dissolved out with strong nitric acid, and the tube, after cleaning and drying, reweighed, the difference giving the weight of metallic arsenic. The results are said to be very satisfactory.

3. *Influence of Organic Matter on the Separation of Arsenic*.—Boeke in a recent paper on the detection of arsenic in organic mixtures, makes the following statement, which the authors consider to be erroneous:—"The admirable method of Marsh in its improved form allows the detection of the minutest trace of arsenic, even in the most complicated mixtures, but with one restriction, viz., that the solution to be examined be wholly free from organic matter." Care must naturally be taken that the acid does not flow into the generator too rapidly, especially if at all concentrated, as it may thereby produce an uncontrollable frothing; however, the presence of a small quantity of sweet oil, which the authors allow to flow down the side of the generator after the zinc has been placed in it and floats on the top of the liquid, is sufficient to prevent any troublesome frothing. D. B.

Detection of Small Quantities of Platinum. By F. FIELD (*Chem. News*, 43, 75).—The following reaction is made use of:—

By adding potassium iodide in slight excess to a solution of platinum chloride, the platinum iodide is dissolved, and, should the solution be concentrated, a red liquid, almost approaching to black, is produced. It was found that one part of the platinum could be detected in two millions of liquid. The colour is destroyed by sulphuric acid, sulphite and thiosulphate of sodium, sulphurous acid, mercuric chloride, and other reagents; also when the coloured solu-

tion is heated. Experiments were made on the detection of platinum when in combination with other metals, solutions being prepared in which the platinum was in the proportion of one to a thousand, and in many cases much less. The following compounds gave satisfactory results:—Zinc and platinum, iron (as a ferrous salt) and platinum, cadmium and platinum, manganese and platinum, cobalt and platinum, lead and platinum, copper and platinum, mercury and platinum, silver and platinum, and gold and platinum. D. B.

Relation between the Oxygen and Organic Matter found in Natural Waters. By T. WEYL and X. ZEITLER (*Zeitschr. f. Physiol. Chem.*, 5, 10—12).—The oxygen was estimated by Schützenberger's method, the organic matter by permanganate. The authors conclude from their experiments that there is no special relation between the oxygen and organic matter, although, as a rule (with some remarkable exceptions), as the organic matter rose, the oxygen fell. They are of opinion that the quantity of oxygen present as gas in water affords no criterion of its quality. W. N.

Apparatus for Studying the Diffusion of Carbon Bisulphide in the Ground. By F. KOENIG (*Gazzetta*, 11, 57—65).—The author describes a very ingenious but somewhat complex apparatus, by means of which about 20 c.c. of air are aspirated from any part of the ground and then submitted to the action of a minute quantity of triethylphosphine. The manner of using the apparatus is, however, very simple, the whole operation requiring only about five minutes. The test is merely qualitative, but some idea of the amount of carbon bisulphide present in the air may be formed from the larger or smaller quantity of the red crystalline compound of carbon bisulphide and triethylphosphine which is formed. The author proposes to employ this method for ascertaining whether the unsuccessful application of carbon bisulphide in some cases to phylloxera is to be attributed to the imperfect diffusion of the insecticide. C. E. G.

Examination of Petroleum. By F. SKALWEIT (*Chem. News*, 43, 76—78).—It was found that the various kinds of petroleum which, at a lower temperature, develop inflammable gases, have a sp. gr. under 0.800 and even 0.789, whereas good sorts are considerably heavier and rise to 0.824. The boiling points also are considerably lower; and it is clear that the inflammability of such petroleum depends, to some extent, on its boiling point. The angle of refraction was determined by making use of Abbé's refractometer. The experiments were made at a temperature of 17° to 18°. The index of the alidade was so adjusted that water at this temperature showed an average of $n = 1.3330$ from both results. A great difference in the index of refraction was obtained with various kinds of petroleum; its regularity in rising and falling, compared with the igniting point, is also exhibited. The igniting point corresponds most with the sp. gr. and the boiling point. This becomes particularly evident when the distillates of petroleum, boiling at a low point, are separately examined. Thus petroleum, for which a sp. gr. of above 0.800 and an

igniting point of 38° is sufficient, has an angle of refraction of 1.4489. With some practice this examination is very simple, and requires a few minutes' time only. Most chemists are likely to prefer it to any other process, for as it is, it gives a clue to find out its usefulness or its defectiveness. If, however, in examining petroleum, its physical properties are entirely left aside, and importance is attached solely to its quality of igniting and burning, the apparatus must be self-acting and sufficiently safe. The author has devised an apparatus for determining the flashing point of petroleum, which is said to be extremely simple in construction, while the results produced are most favourable, and do not vary with the same sample. D. B.

Notes on Petroleum Spirit and Allied Liquids. By A. H. ALLEN (*Chem. News*, 42, 189).—The following table exhibits in a convenient form the physical characters of the volatile naphthas from petroleum, shale, and coal-tar, together with the differences observed in their solvent action on coal-tar pitch, and anhydrous crystallised carbolic acid:—

	Petroleum spirit.	Shale naphtha.	Coal-tar naphtha and benzol.
a. Leading constituents.	Heptane, C_7H_{16} , and its homologues.	Heptylene, C_7H_{14} , and its homologues.	Benzene, C_6H_6 , and its homologues.
b. Sp. gr. of sample at 15.5° .	0.690	0.718	0.876
c. Boiling point of sample.	$55^{\circ}C$.	$56^{\circ}C$.	$80^{\circ}C$.
d. Solvent action of the sample on coal-tar pitch.	Very slight solvent action. Liquid only coloured amber-yellow after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
e. Behaviour on agitating three measures of sample (cold) with one measure of fused crystals of pure carbolic acid (Calvert's No. 2).	No apparent solution. The liquids are not miscible.	The liquids form a homogeneous mixture.	The liquids form a homogeneous mixture.

The following table shows roughly the differences in chemical composition between commercial petroleum-products and the bodies of similar physical characters obtained by the distillation of shale as deduced from the action of nitric acid on the oil:—

Product.	Petroleum.	Shale.
Naphtha or spirit; sp. gr. about 0.700; boiling point about 56° C.	At least 75 p. c. of hydrocarbons of the paraffin or marsh-gas series, C_nH_{2n+2} . The remainder olefines, C_nH_{2n} , with distinct traces of benzene and its homologues.	At least 60—70 p. c. of hydrocarbons of the olefine or ethylene series, C_nH_{2n} . The remainder paraffins, C_nH_{2n+2} . No trace of benzene or its homologues.
Photogene or burning oil; sp. gr. about 0.800; boiling about 160° C.	55—80 p. c. of higher members of the paraffin series, C_nH_{2n+2} . The remainder chiefly olefines.	60—65 p. c. of higher members of the olefine series, C_nH_{2n} . The remainder paraffins.
Lubricating oil	?	Almost wholly higher olefines, C_nH_{2n} , the paraffins of similar high boiling point being solid. No naphthalene.
Wax	Solid paraffins, C_nH_{2n+2} . . .	Solid paraffins, C_nH_{2n+2} .

D. B.

Rapid Alcoholic Fermentation. By J. BOUSSINGAULT (*Ann. Chim. Phys.* [5], 22, 98—120).—In the course of difficulties which arose in the determination of glycerol present in certain wines from the International Exhibition of Paris, 1878, the author proposed to destroy the sugars present by fermentation with fresh yeast. On adopting this process in a specimen of rancio from the Pyrenees (containing a large quantity of sugar), however, it was found that although the fermentation, by the addition of the yeast, was violent at first, then moderate, all the sugar was not destroyed, even after several days. This phenomenon may be attributed to the quantity of alcohol originally present in the rancio, and also to the alcohol gradually accumulated by the fermentation as observed by Chevreul. In order to eliminate the alcohol and carbonic acid formed, the vessel containing the fermenting wine was connected with an air-pump; under these conditions all the sugar in the same specimen of rancio had completely disappeared at the end of six hours. Comparative experiments were then made with two flasks containing the same wine, with the same quantities of water and yeast added, and the fermentation carried on at the same temperature; but one kept at ordinary, the other at reduced pressures. In all cases the fermentation in the latter was more rapid than in the former. The same phenomenon was observed when artificial mixtures of glucose (or sugar), alcohol, and water were fermented, the action of the yeast being moderated, even when the alcohol produced by the fermentation did not exceed 2 per cent. of the liquid fermented. Experiments are quoted to show that the fermentation is completely stopped when the accumulated alcohol is in a sufficiently large proportion. It is also proved that a solution of glucose in water ferments with greater rapidity than a solution of glucose (of the same relative strength) in alcohol at ordinary temperatures; and that solutions of glucose in alcohol ferment more rapidly the lower the pressure. In the analysis of wines containing a large proportion of sugars, it is further

necessary to destroy the latter by a rapid fermentation in order to estimate the glycerol and succinic acid present. But the author shows that glycerol is a product of the fermentation of sugar, even with a rapid fermentation excited by a high temperature, the addition of a large quantity of yeast, and a reduced pressure, the sugar yielding as much as 2·5—3·6 per cent. of its weight of glycerol. He considers it probable that in the above conditions there is formed a greater quantity of the various products of the normal fermentation of alcohol; but this point is not further examined.

V. H. V.

Specific Rotatory Power of Cane- and Invert-sugar. By A. H. ALLEN (*Chem. News*, 42, 177).—The formula commonly used for calculating the apparent specific rotatory power of optically active

bodies in solution is as follows:— $S = \frac{a}{l \times \frac{c}{100}}$. The author has

substituted S for the symbol $[\alpha]$ in this formula, which is usually used to denote specific rotatory power; a is the angular rotation observed; l the length of the solution traversed by the ray of light; and c is the concentration of the solution. It was found that the true quantity of cane-sugar to be taken for use with Soleil's saccharimeter is 16·26 grams, and not 16·19 or 16·35, as sometimes given. The value of S for cane-sugar, according to numerous observers, is $+73·8 =$

$\frac{24c}{2 \times \frac{c}{100}}$; whence $c = 16·26$. If it be contended that either of the

above alternative quantities is the right one to employ, then it follows that $+73·8^\circ$ is not the true value of $[\alpha]_D$, or S_D , for cane-sugar, although this is the figure used in all books. In calculating the specific rotatory power of invert-sugar, the author thinks that Watts and others appear to have assumed that a solution of inverted sugar after correction for change of bulk, contained the same percentage of solid as before inversion. This is not the case, 95 parts of cane-sugar yielding 100 parts of invert-sugar. Thus, according to the

data already given, at a temperature of 15°C , $S_D = \frac{-36·5 \times 0·24}{2 \times \frac{16·26}{95}}$

$= -25·6^\circ$. This number corresponds with a value of $-25·94^\circ$ for S_D at 14°C , instead of 25° , as is generally assumed. If the number 16·19 be adhered to as the normal weight of sugar per 100 c.c., this

value becomes $S_D = \frac{-37 \times 0·24}{2 \times \frac{16·19 \times 100}{100 \times 95}} = -26·05^\circ$ at 14°C , against

-25° as generally taken. The following corrected values are given:—

	Cane-sugar.	Invert-sugar.	Dextrose.	Levulose.
$S_D =$	$+73·8^\circ$	$-25·6^\circ$ at 15°C .	$+57·6^\circ$	$-108·8$ at 15°C .

D. B.

Specific Rotatory Power of Cane- and Invert-sugar. By A. WATT (*Chem. News*, **42**, 196).—Referring to the paper abstracted p. 653, the author mentions that it is highly improbable that any one who had occasion to make a calculation of the specific rotatory power of inverted sugar should omit the very obvious correction pointed out by Allen. Moreover, an error of the kind indicated above, instead of giving -25° , gives a number even *higher* than that given by Allen as the corrected one. He obtains the value -25.6° at 15° for $[\alpha]_j$ from the formula—

$$[\alpha]_j = \frac{-36.5 \times 0.24}{2 \times \frac{16.26}{95}} = -25.6^\circ,$$

Omitting the correction, the formula gives—

$$[\alpha]_j = \frac{-36.5 \times 0.24}{2 \times \frac{16.26}{100}} = -26.93^\circ$$

-26.93° instead of -25° as Allen supposes.

The author states that the value -25° given by Watts and others is the *calculated* specific rotatory power of invert-sugar, and not the *observed*. As shown by Kekulé, it is the mean of the *observed* rotatory powers of dextrose $+56^\circ$ (Berthelot), and levulose -106° (Dubrunfaut), calculated on the assumption that invert-sugar consists of equal parts of dextrose and levulose, thus—

$$\frac{-106}{2} + \frac{+56}{2} = -25^\circ.$$

This mode of calculation Allen evidently does not consider erroneous, as he uses it in order to obtain the value for levulose.

D. B.

Detection of Starch-sugar Mechanically Mixed with Commercial Cane-sugar. By P. CASAMAJOR (*Chem. News*, **42**, 326).—Some time ago the author gave several processes for the detection of starch-sugar in commercial sugars. One of these consisted in adding to the suspected sugar a quantity of cold water, somewhat less than its own weight, and stirring the mixture for a few seconds. If starch-sugar is present, it will be seen in the shape of white chalky specks. The author recently examined a sample of yellow refined sugar supposed to be adulterated by being mixed with starch glucose. By applying the test, he repeatedly obtained a few small chalky specks, which dissolved after standing a minute or two, making it very uncertain whether any starch glucose was present. It was found, however, that methylic alcohol of such density as to mark 50° by Gay-Lussac's alcohometer answered the purpose of dissolving the sugar very well, if previously saturated with starch-sugar; this solution dissolves cane-sugar, either white or yellow, very readily, but does not dissolve starch-glucose. The author has not had occasion to determine experimentally the degree of approximation obtainable by working with methylic

alcohol, and the above is therefore merely a suggestion to those who may require quantitative results. D. B.

Quantitative Estimation of Glycogen. By E. KÜLZ (*Pflüger's Archiv*, **24**, 90—94).—A slight modification of Brücke's gravimetric method is recommended. W. N.

Testing of Phenol. By E. WALLER (*Chem. News*, **43**, 151—153).—The qualitative and quantitative tests for phenol are fully described.

In the qualitative solubility test, after shaking the phenol with water, the author adds olive oil to facilitate the separation of the insoluble portion from the aqueous solution.

The estimation of phenol with bromine-water is effected by treating the phenol with bromine-water previously standardised to a 1 per cent. solution, so that 3 c.c. of the former equal 1 of the latter. Bromine water is then added so long as a precipitate is formed. The coagulation of the precipitate as it forms is brought about by shaking with a saturated solution of alum in dilute sulphuric acid.

L. T. O'S.

Tartaric Acid Reaction. By H. J. H. FENTON (*Chem. News*, **43**, 110).—The reaction is brought about by adding to a solution of tartaric acid or alkaline tartrate a small quantity of ferrous sulphate or chloride, followed by one or two drops of hydrogen peroxide, and finally an excess of potash or soda. A beautiful violet colour is thus obtained, which in very strong solutions appears almost black. At first sight, it seemed probable that this colour was due to the formation of an alkaline ferrate. This explanation was not, however, supported by further experiments. The solution may be evaporated to dryness in a vacuum without losing its properties, which are evidently due to some products of the decomposition, or perhaps direct oxidation, of tartaric acid. This reaction may also be produced by electrolysing a solution of tartaric acid, using an iron plate for the positive electrode. The liquid around this plate turns yellow, and if now a solution of potash be added, the violet colour at once appears. As a test for the identification of tartaric acid, this reaction is said to be one of easy application and of average delicacy. It is necessary, however, to avoid the presence of heavy metals and of oxidising agents before applying it. The author is working with this violet substance with a view of isolating it. D. B.

Quinoline Reactions. By A. KRAKAO (*Ber.*, **14**, 599—602).—A disputed claim for priority.

New Guanine Reaction. By S. ST. CAPRANICA (*Zeits. f. Physiol. Chem.*, **4**, 233).—Warm solutions of guanine hydrochloride give with solutions of picric acid (saturated in the cold) an orange-red crystalline very insoluble precipitate. Xanthine and hypoxanthine give this reaction only in very concentrated solutions, whilst very dilute solutions of guanine show the reaction readily.

Potassium chromate (whether neutral or acid salt is not stated by the author) gives a crystalline orange-red, and potassium ferricyanide a yellow-brown crystalline precipitate.

W. N.

Estimation of Fat in Milk. By W. M. HAMLET (*Chem. News*, **43**, 170—171).—After a general review of the various processes for the estimation of milk fat, the author describes the following modification of Church's method:—

5 or 10 c.c. of milk are evaporated to dryness over a water-bath in a thin metallic or glass dish, the residue being granulated by stirring or addition of alcohol or acetic acid. The residue in the dish, which is cut or broken in pieces, is transferred to an extractor consisting of a Liebig's condenser with a wide central tube, drawn out at one end to a small bore. This end is inserted in a cork and fitted to a flask; a plug of cotton wool is placed in the tube, the residue and broken dish packed in and covered with another plug of cotton wool. The fat is extracted four times with ether, the extract freed from ether, dried, and weighed.

This furnishes results higher than are obtained by Wanklyn's method.

L. T. O'S.

Aräometric Method for the Estimation of Fat in Milk. By F. SOXHLET (*Chem. News*, **43**, 101—104, and 111—112).—The author states that for the estimation of the most important constituent of milk—the fat, only one method has proved satisfactory, namely, the gravimetric method. The principle of his method, which forms the subject of the present paper, does not occur in any of those in use. It is as follows:—Known quantities of milk, caustic potash solution, and ether, are shaken together; the fat, as is known, dissolves completely in the ether, which, after standing for a short time, rises to the surface. A small portion of the ether, which is always constant, remains dissolved in the alkaline solution, but does not contain any fat, as the ether in the water does not dissolve the slightest trace of fat. The remaining portion of the ether forms with the fat a solution whose concentration varies as the amount of fat present in the milk. The concentration of this ethereal solution of fat can be ascertained by the estimation of its specific gravity with as certain and accurate results as those obtained by estimating the amount of alcohol in an aqueous solution with the alcohometer, as the difference between the specific gravity of fat and ether is as great as between that of water and alcohol. The process proposed by the author is based on the supposition that the specific gravity of milk-fat is constant, or only fluctuates to a very small extent. Another supposition is that the same amount of ether is always dissolved by the milk, so that the quantity of ether which forms the ethereal solution is always constant. A large portion of the paper is occupied in describing the apparatus and manner of procedure, and comparative tables are appended to the paper, showing the difference in the results obtained by the author's aräometric method and the ordinary gravimetric method.

D. B.

Milk-testing with the Lactobutyrometer. By G. C. CALDWELL and others (*Bied. Centr.*, 1880, 905—907).—This paper consists of extracts from the report of the Cornell University Experimental Station, Ithaca, N.Y., where the instrument has been used to estimate the fat in milk. Caldwell has found it to agree with chemical analyses within $\frac{1}{10}$ to $\frac{1}{5}$ th of a per cent., rarely differing more—the difference on the results of a week's experiments was :—Analyses, average 3·3 per cent. ; instrument, 3·35 per cent.

With cows fed on bran, the correspondence was not so constant. For example—

Analyses	4·12	4·54	4·85	3·20
Instrument	3·79	3·99	4·12	3·05

On another occasion the averages were :—Analyses, 4·04 per cent. ; instrument, 3·4 per cent. The author found more regular results when a few drops of acetic acid were added to the sample, and thinks the instrument in question the best that has been introduced, and most trustworthy when the operator wishes to avoid delicate weighings and manipulation.

Jenssen has tried the lactobutyrometer with many samples. He finds two-thirds of the observations show lower, and one-third higher results than analysis. Friedländer, Schrodtt, and Schmöger, as the result of their comparisons, find in some cases no difference, but very remarkable ones in others. J. F.

Milk Analysis. By N. GERBER and others (*Bied. Centr.*, 1880, 899—905).—The authors say that in an exact milk analysis, the sample should be weighed and not measured, as frequent differences of weight arise with the same measured quantity of milk ; they give examples in proof. They do not recommend the common method of drying the milk with sand, but advise it to be previously coagulated with alcohol or acetic acid, and then dried without sand ; in four experiments, according to each method, with three samples of milk, there was a difference of 1 per cent. in the sand process, and only $\frac{1}{10}$ per cent. with the other. The authors condemn other systems altogether. They weigh the sample in a platinum dish covered with a watch-glass ; it is then coagulated with a few drops of alcohol or acetic acid, evaporated on a water-bath, the coagulum while damp divided against the sides of the dish, and then thoroughly dried at 100—110°, weighed every two hours, and at the end of six hours the weight is generally found constant. The ash is also determined in this sample. For the estimation of protein matter and fat, the authors follow the method of Ritthausen, viz., 10 c.c. of the milk is diluted with 100 c.c. distilled water, and well mixed ; a copper solution is then added slowly with stirring, until the coagulum commences to settle quickly. The copper solution consists of 63·5 cupric sulphate in 1 liter of water, of which 10 c.c. = 0·2 gram CuO. The whole is then, with one-half the quantity of cupric solution first employed, added to a potash solution of 50 grams K₂O in a liter of water ; the mixture should react but slightly acid or completely neutral. After a short interval the clear fluid is

filtered off through a filter dried at 110°; the precipitate is then brought on the filter and washed with 100 c.c. water, continued until the wash-water amounts to 240 c.c., which, made up to 250 c.c., serves to estimate the milk-sugar in.

The coagulum on the filter is treated with absolute alcohol until it hardens; it is then slowly dried and extracted with ether, the ether and alcohol distilled off, and the fat dried and weighed. The coagulum is then dried at 125°, weighed, and ignited, the ash deducted, and the remainder taken as pure albuminoid or protein. The milk-sugar is estimated in the before-mentioned filtrate from the albuminoid by Fehling's solution, the strength of which is 1 c.c. = 6·7 mgrms. of milk-sugar.

The author has examined the milk of various animals. Human milk requires more of the copper solution to coagulate it. Mare's, goat's, and ewe's milk he analysed in the same way as cow's milk, with the following results:—

	Water.	Salts.	Fat.	Albumi- noids.	Milk- sugar.	Sp. gr.
Cow's milk skimmed..	90·52	0·77	0·29	3·84	4·20	1·0350
Mare's milk	91·76	0·31	0·39	2·45	5·99	1·0360
Goat's milk	90·16	0·73	2·29	2·95	3·97	1·0290
Woman's milk	88·73	0·29	3·24	3·56	4·20	1·0294

Condensed milk is treated as follows:—2–3 grams are weighed off in a covered beaker, dissolved in 100–150 c.c. water, decomposed with copper solution sufficient to quickly precipitate the coagulum, a little potash solution added (1·5–2 c.c. copper solution, 0·7–1 c.c. alkali), and the analysis continued in the same manner as fresh milk.

A number of analyses of different condensed milks are given; the albuminoids exceed fat and milk-sugar. A specimen is given:—

Locality of manufacture.	Fat.	Albu- minoids.	Milk-sugar.	Cane-sugar.
Thun	10·42	12·46	11·04	38·14
Vevey	11·53	12·67	11·19	37·69
Cham	9·70	11·35	11·95	41·41

Vogel weighs his samples also, but in closed weighing tubes, having found a loss of water amounting to as much as 17 mgrms. in a weighing lasting 5 minutes when carried out in open vessels. He estimates total solids and fat by drying in tinware dishes of an oblong shape, which can be placed, with the residue, intact into the Soxhlet extraction apparatus, avoiding loss in removal, and offering control of the fat percentage found by ordinary methods.

Janke's contribution to the paper under abstract is a report of a

series of examinations of the milk supplied to the city of Bremen, more than 250 samples being examined, some of them very bad, viz. :—Total solids, 7·71 per cent. ; 6·80 per cent. ; 8·23 per cent. ; and fat, 0·868 per cent., 0·633 per cent., 0·416 per cent. ; and what is strange, the samples in question were stall samples, taken from the cow, in presence of a police officer.

Dr. Tollens in a note to this part of the communication, repeats a caution frequently given by him, against pronouncing milk to be adulterated by addition of water or removal of cream, when such figures are obtained from milk drawn fresh from the cow, but again recommends the use of the words good, middling, bad, very bad, and publication of the vendor's name.

Jancke's method of analysis is to weigh off 10 grams, and add to it 20 grams sea-sand, evaporate in a Hofmeister bulb of thin glass, and cool in desiccator ; another 10 grams without sand are also dried and weighed. The residue in the bulb is placed in a mortar, which is covered with a glass plate, having a hole for the handle of the pestle, pulverised, mixed with dry marble, transferred to a tube closed with a cotton wadding plug, and extracted with ether ; the other residue, without sand, is extracted in a Soxhlet apparatus. The author can do 20—25 milk analyses in two days by this method. J. F.

Detection of Aniline Colours in Red Wine. By H. MACAGNO (*Chem. News*, 43, 169—170 ; from *Gazzetta*, 11, 114—120).—Aniline colours in red wines may be detected spectroscopically, since a natural wine diluted with 2 vols. of water gives no defined bands, but a hazy absorption from F to the end of the violet, which does not interfere with the characteristic bands of the aniline colours. After dilution with water, a few drops of acetic ether are added, by which the cenolin is slightly dissolved. A table showing the position of the spectrum in which absorption takes place is given. By this method 0·005 gram per litre of aniline colour can be detected. L. T. O'S.

Identification of Coal-tar Colours. By J. SPILLER (*Chem. News*, 42, 191).—The author mentions that if the colouring matter under examination is dissolved in strong sulphuric acid, a colour-test is at hand, whereby useful inferences may be derived as to the nature of the dye, and its identity exactly determined in many cases. A few direct confirmatory tests may then be applied. The most remarkable colour reactions with sulphuric acid are the following :—

Magdala (naphthalene pink) ..	Blue-black.
Saffranin	Grass-green, becoming indigo-blue on strongly heating.
Crysoïdin	Deep orange, turning almost to scarlet on heating.
Alizarin	Ruby-red or maroon.
Eosin	Golden-yellow.
Primrose (naphthalene yellow).	Sparingly soluble, first yellow, and colour discharged on heating.

Crysaniline	Yellow or brown solution, of marked fluorescent character.
Aurin.....	Yellowish-brown, non-fluorescent.
Atlas orange	Rose colour, turning scarlet on heating.
Atlas scarlet.....	Scarlet solution, very stable on heating.
Biebrich scarlet, R	Blue-black or deep purple.
B	Bluish-green.
Aniline scarlet	Golden - yellow, permanent on heating.
Indulin	Slatey-blue to indigo, according to shade of dye.
Rosaniline, regina, and violets.	Yellow or brownish-yellow.
Phenyl and diphenylamine blues	Dark-brown solutions.
Iodine green	} Bright yellow solutions, the former giving off iodine on heating.
Malachite green	
Citronine	Pale cinnamon or neutral tint.

D. B.

Quantitative Estimation and Separation of Protein Matter in Plants. By A. STUTZER (*Bied. Centr.*, 1880, 875—878).—Ritt-hausen was the first to point out that protein formed insoluble combinations with cupric oxide, and he founded on the fact a method for the estimation of protein in milk. His process, however, requires exact neutralisation by an alkali, which causes certain inconveniences. The author has devised an improvement by employing a perfectly neutral alkali free hydrated oxide of copper, prepared as follows:—Very dilute cupric sulphate solution is decomposed with very dilute soda solution to alkaline reaction, the precipitated cupric hydrate thrown on a large filter, quickly washed, the filter pierced, and the substance washed into a flask, which is then filled with cold water and washed by decantation until the wash-water is perfectly neutral. The precipitate is drained on a filter, dried between filter-paper, and then rubbed up with water or alcohol into a thick semi-fluid condition.

To test the accuracy of the method, the author made a combustion of pure palm-nut meal by the soda-lime process. 1 gram of the same meal was then treated with 100 c.c. water and heated to incipient boiling, the reagent added, the precipitate separated, washed with hot water, and then twice with absolute alcohol to remove moisture, dried at 100° C., and ignited with soda-lime (the nitrogen in the filter being known). The figures obtained agreed with those from the direct combustion of the original sample.

The next step was to discover the value of the method for separation of protein from other nitrogenous substances. The method pursued was to mix a portion of the palm meal, the protein in which was known, with those substances. If the nitrogen was greater in amount than in trials with the meal alone, it must of necessity have been derived from the added substances; if it remained constant, the separation of the protein from the other nitrogenous matter was successful.

The separation from nitrates, ammonium salts, amygdalin, and asparagine took place easily; less easily from solanine, leucine, tyrosine.

A series of experiments was made with caffeine, morphine, and narcotine; but it was found that the presence of tannin interfered with their quantitative estimation, although when they were present in the free state or combined with other acids, it was easy. As the presence of tannin in the plant is unavoidable, the following modification of the process is recommended:—The tannin compound is decomposed by adding to the sample in a beaker a mixture of 99 c.c. absolute alcohol, with 1 c.c. acetic acid, warming the mixture, decanting from the quickly-formed precipitate, which is then treated with absolute alcohol, and the remainder of the process carried out as before described. This method has been found successful in the cases of solanine, leucine, and tyrosine, which in former cases did not give such favourable results. J. F.

Quantitative Analysis of the Albuminoids of the Kidney Substance. By E. GOTTWALT (*Zeitschr. f. Physiol. Chem.*, **4**, 437).—After thorough washing with 0.75 per cent. sodium chloride solution to get rid of the blood, the author obtained albuminoids from the finely-divided substance as follows. Mean of six experiments, all of which agree fairly well:—

Serum albumin, 1.251 per cent.; globulins, by Hammarsten's method, 3.818 per cent.; total albumin in the extract, 5.069. Albumin extracted by salt solution (10 per cent.), 5.232 per cent.; albumin soluble in sodic carbonate, 1.524 per cent.; mucin, 1.016 per cent.

W. N.

Analysis of Shoddy and Wool Waste. By J. HUGHES (*Chem. News*, **42**, 325).—The author mentions that for some time past it has been the practice for manure manufacturers to purchase shoddy at so much for each unit of ammonia per cent. per ton, the ammonia being calculated from the yield of nitrogen as determined by the usual combustion process with soda-lime. If the samples are fairly drawn, carefully prepared for analysis, and the analytical operations be skillfully performed, the results obtained should agree, and the difference in the ammonia determinations of duplicate samples should not be greater than one or two-tenths per cent. However, the difference between the percentage of ammonia found by the seller's chemist and that found by the buyer's chemist frequently amounts to as much as 1 or even 2 per cent., and a very serious loss is therefore incurred by one of the two parties to the contract. With a view of removing such discrepancies, the author suggests the following modifications:—

1. That samples of shoddy should be drawn as fairly and impartially as possible; that the buyer and seller's representative respectively should not be allowed to select samples, but that official samples should be taken by a lad (blind-folded, for a wool dealer would almost unconsciously select a superior quality for his sample).

2. That each sample should consist of at least one pound, that four of such one pound samples should be drawn, placed in wide-mouthed jars or bottles and officially sealed; two samples being given to the buyer and two to the seller.

3. That the chemist be requested to state on the analysis certificate the proportions of water and (nitrogen equal to) ammonia found in the sealed samples as received.

D. B.

Technical Chemistry.

Preparation of Pyrogallol for Dry-plate Development. By T. E. THORPE (*Chem. News*, **43**, 109).—Ten grams of dry gallic acid and 30 c.c. of glycerol are placed in a two-ounce flask or wide test-tube, and heated on a sand-bath at a temperature of from 190° to 200°, so long as bubbles of carbonic anhydride are seen to be formed in the liquid. The gallic acid readily dissolves, and is converted entirely into the theoretical quantity of pyrogallol. The brown viscous liquid, after cooling, is diluted with 1,000 c.c. of water, which forms a solution, each half ounce of which contains rather more than one and a half grains of pyrogallol, sufficient therefore for developing a quarter-plate, according to Swan's instructions. In containing glycerol, it resembles Edwards' solution which has found favour with many photographers.

As the price of pyrogallol is about seven times that of gallic acid, it is thought that the above process may be worthy of the attention of photographers who practise alkaline development. D. B.

Chemistry of Sewage Precipitation. By W. WALLACE (*Chem. News*, **43**, 55—57, 67—68, and 90—91).—A great deal has been said and written about the purifying action of water, but the author points out that water *per se* has no purifying action whatever. By mixing excreta with pure or boiled water, it would certainly be diluted; but the water would not prevent its decomposition and consequent offensiveness in the slightest degree. The oxygen in common water exerts a most powerful influence on sewage, but it requires an enormous volume to yield sufficient oxygen to render innocuous a very small quantity of excreta.

There are two ways in which excremental matter may be dealt with; the dry system and carriage by water. The first is the most rational, as well as the most consistent with public health and national prosperity. The weak part of this system is, that whilst it disposes of excreta, it leaves untouched all other kinds of sewage, which still require to be removed by means of water-carriage, and demand the same purification before passing into a river as the excreta themselves. When water-carriage is used, the following methods may be employed for the disposal of the sewage:—

1. Running it into the sea, or into a tidal river under conditions that will prevent its return.

2. Irrigation.

3. Purification by precipitation.

- a. By lime.

b. By sulphate of alumina.

c. By the A.B.C system.

In considering the purification of the sewage from different towns, the author mentions that by using it in the irrigation of land, about an acre is required to each 100 of population; in Glasgow, therefore, fully 10 square miles of land would be taken up. Several processes have been advocated for purifying sewage by precipitation, and at the same time manufacturing from the sludge obtained a manure which will be saleable at a considerable price, under the name of native guano. The purification of the sewage is possible, and has been carried out successfully at Bradford, Leeds, Coventry, Birmingham, and many other towns; but the sale of the so-called manure, except in insignificant quantities, appears to have failed of accomplishment. The precipitant, whatever it may be, while it removes the solid matter of the sewage, together with the phosphoric acid, leaves in the effluent water all or nearly all the ammonia and the potash salts, these constituting by far the most valuable part of the sewage.

The matters removed by lime and by alumina, which are practically the only precipitants that have hitherto been employed, are:—Solid matters, phosphoric acid, fatty acids of soaps, nitrogenous organic matters, vegetable colouring-matters, magnesia. The soluble nitrogenous compounds and the ammonia in the effluent soon become oxidised, less rapidly in salt than in fresh water; and the oxidation is greatly facilitated by passing the purified sewage through a porous material, with free exposure to the air, or through sandy or gravelly soil.

Of all the substances proposed for precipitation, the one that appears to be most capable of general application is lime, as it can be had everywhere, is cheap, and effects a sufficient purification to enable the effluent to be passed into a non-potable running stream or tidal river, especially if the precipitation is supplemented by filtration through some form of charcoal, or by running it over a limited extent of suitable land, thoroughly drained.

Among the towns where precipitation is in use, none is more worthy of attention than Leicester, the population of which is about 120,000, while the sewage amounts to 7,000,000 gallons per day. The quantity of lime used is 20 to 30 cwts. per million gallons, and nothing is obtained for the sludge, which has hitherto been employed, almost exclusively, in making up land in the immediate neighbourhood of the works. The cost of working, for lime, fuel, and labour, is £2,200 per annum. The whole of the sewage requires to be pumped 26 feet. The precipitation is effected in a series of very large tanks and settling ponds, and the effluent is further purified by filtration through an osier bed three acres in extent.

Coventry has been working for some years under Dr. Anderson's patent, in which sulphate of alumina, with enough lime to throw down the alumina, is employed. The quality of the salt is of the crudest and poorest description, and as the effluent is very good, it shows that a material of the cheapest kind may be successfully employed. The process, under any circumstances, must involve a greater outlay than if lime is employed, but the author considers that this is

counterbalanced to a very considerable extent by the diminished quantity of sludge to be disposed of. If the phosphoric acid be accepted as the measure of the manurial strength of the sludge, it will be seen, on comparing the various analyses, that the article produced in works where sulphate of alumina is the precipitant, is from twice to three times as strong as that precipitated by lime.

It is stated that whatever system of precipitation is adopted, the disposal of the sludge is one of the most important elements in the calculation of cost. The author has estimated that the sewage of Glasgow—40,000,000 to 70,000,000 of gallons daily—will produce a quantity of sludge which in the dried state would amount daily to 135 tons; but as it must be dealt with in its moist condition, it would be a fair estimate to take five times this, or 675 tons. If lime alone were used as the precipitate, an average of about 40 tons would be required daily. The total cost of working the precipitation process, not including interest on works, would probably amount to about £25,000 per annum.

The author concludes, from a series of experiments made with Glasgow sewage, that the latter, properly defecated and introduced into the Clyde at a point below the city, will not, under any circumstances, give rise to a nuisance.

The question whether lime or alumina is the more effective agent for the precipitation of sewage, has engaged the author's attention, and his observations appear to indicate that, although the alumina produces a somewhat more satisfactory effluent, the advantages obtained by its use are not sufficient to compensate for the greatly increased cost of purification, which may be set down at about four times that of lime. If, however, a cheap variety of sulphate of alumina, with some sulphate of iron, can be obtained, or if the liquor obtained by lixiviating calcined alum shale is available, if, in fact, the cost of alumina, or a mixture of alumina and oxide of iron, could be made approximately that of lime, the author would have no hesitation in recommending its use in preference to lime.

D. B.

Nitric Oxide a Disinfectant. By H. SULLIOT (*Bull. Soc. Chim.* [2], 35, 356—357).—The author has applied the experiments of C. Girard and Pabst (this Journal, 36, 333) on the lead chamber crystals, to deodorising the gases from cesspools by passing the gases into towers filled with coke, down which trickles sulphuric acid containing 3 to 4 per cent. of the chamber crystals. The moisture of the gases is sufficient to decompose the crystals, the nitric oxide of which decomposes the gases. For the disinfection of rooms, nitric oxide mixed with the vapour of ethyl nitrite may be used, the latter counteracting the irritating effects of the former. The mixture is effected by placing some crystals of nitrosulphuric acid in a porous vessel, which is inserted in another containing alcohol.

L. T. O'S.

Manufacture of Sodium Sulphate by the Direct Process. By J. HARGREAVES (*Chem. News*, 42, 322—324).—The author gives a description of the manufacture of sodium sulphate by the "Hargreaves and Robinson direct process," first made known about ten years ago,

showing its slow but sure progress, and confining himself to its technicalities.

The following are the advantages claimed :—

1. Although the cost of apparatus is about the same as that required for the old process, there is this difference: that, whereas the life of a vitriol chamber may be estimated, say at 10 years, the cylinders used with ordinary care in the direct system show every sign of lasting three times that period without renewal.

2. Less fuel, being about one-half that required by the old process.

3. Less labour, and with the exception of the burner men, and one intelligent person to look after the plant, no skilled labour is required.

4. Less repairs. This item is less than 6*d.* per ton of sulphate made.

5. No nitrate of soda is necessary.

6. Cheaper qualities of salt—not available for the old process—can be used.

7. Less sulphuric acid amongst the hydrochloric acid, consequently less annoyance from calcium sulphate in the Weldon process.

8. No leakage of hydrochloric acid into the fire flues, the whole of it passing through exhausters.

9. The sulphate, when drawn, emits no hydrochloric or sulphuric acid to annoy the workmen.

10. Sulphate is made containing only small quantities of chloride and free acid, and therefore especially adapted for the manufacture of 76 per cent., or other high strength caustic soda, for which it is largely used. It is guaranteed to contain less than 0.5 per cent. of sodium chloride, but often contains less than 0.2 per cent. Sulphate made by this process is also used for the manufacture of plate glass. Lastly, a reduced cost of production, which may be fairly estimated at 15 to 20 per cent.

D. B.

Treatment of Mineral and Other Substances containing Small Quantities of Calcium Phosphate. By C. H. ALLDRED (*Chem. News*, 42, 177).—In trying nearly all the reagents capable of dissolving tricalcium phosphate, the author used a solution of sulphurous acid in water. Although this readily dissolves an artificially precipitated tricalcium phosphate, it does not so easily dissolve that which may be intimately mixed with silicic acid, lime, ferric oxide, calcium sulphate, &c. To overcome this difficulty the following plan was tried:—The material employed contained about 22 per cent. tricalcium phosphate, 12 per cent. ferric oxide, and the remainder consisted of lime, silica, oxide of magnesium, &c. It was finely ground and placed in a small boiler lined with lead and fitted with a steam-jacket. This was nearly filled with a saturated aqueous solution of sulphurous acid. The boiler was then firmly closed up, and the whole heated until the water in the jacket (which was not under pressure) boiled, and kept at this temperature for five or six hours; it was then cooled and the contents filtered. The filtrate contained nearly the whole of the tricalcium phosphate and only a small quantity of iron. The former can be precipitated either by adding lime, or, better, by boiling, when it is obtained in a fine white powder as a nearly pure “bisulphited” calcium phosphate.

The author mentions that this process, when put into practical application, is very simple, and offers an economical means of treating many substances containing tricalcium phosphate, in quantities too small to pay for treatment by acids, and especially for localities where large deposits of phosphates occur, but too poor to pay for transit in their natural state.

D. B.

Production of Aluminium Sulphate Free from Iron from Aluminous Minerals containing Iron. By J. W. KYNASTON (*Chem. News*, 42, 191—193, and 202—204).—The author mentions that the various aluminous minerals available for the production of salts of this earth are, perhaps, with the single exception of cryolite, invariably contaminated with a greater or less proportion of iron. Inasmuch as the behaviour of oxide of iron towards any of the strong acids is exactly similar to that of alumina, it is not possible to obtain a solution of the latter free from the objectionable impurity; and it is owing to this difficulty that, to meet the demand for a pure compound of alumina, manufacturers have been compelled to produce the readily crystallisable double salts of aluminium and potassium, or ammonium. In the production of these, however, large quantities of potassium or ammonium are required, which are wasted, their presence in the aluminium salts serving no purpose whatever in the uses to which the salt is applied. Bauxite is now very largely used for the preparation of aluminous salts, and several modes have been made known for producing these salts from the mineral. The following is an analysis of the Irish mineral found in the County Antrim:—

	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.
No. 1 ..	49·8	1·45	0·57	0·12	0·01	none
No. 2 ..	51·53	4·53	0·78	0·20	0·02	0·06
	SiO ₂ .	TiO ₂ .	SO ₃ .	P ₂ O ₅ .	H ₂ O combined.	Moisture.
No. 1 ..	8·02	5·37	0·06	trace	27·07	7·50
No. 2 ..	11·89	6·14	0·07	trace	23·79	0·90

The author found that oxalic acid has the remarkable power of dissolving the oxides of iron contained in bauxite to a far greater extent than even strong hydrochloric or nitric acid, and this without any preliminary treatment of the ore, except the necessity of reducing it to a fine state of division. In practice, however, a large plant is required for a small production, although the results are most satisfactory. Nevertheless, this result led the author to the conclusion that the only suitable mode of purification would be one which either prevented the solution of the iron oxides when bauxite is treated with sulphuric acid, or one which effected the separation from the alumina solution of the dissolved iron by some process of precipitation. After a long investigation the author found that ferric arsenite is insoluble in cold solution of aluminium sulphate, if there is present in the solution a small proportion of the tetrabasic sulphate and also a slight excess of arsenious acid. The presence of some tetrabasic sulphate in the solution seems to be essential for the reason that carbonate of

lime (not lime or even caustic alkalis) is the only substance which throws down the arsenite of iron. By the employment of these reactions, it was found possible to remove from a ferruginous solution of alumina, practically all the iron existing in the ferric state, and to produce easily from bauxite a sulphate of alumina, of a far higher degree of purity than has hitherto been produced from the finest quality of china-clay. The removal of a small quantity of ferrous iron remaining in the sulphate of alumina so purified, was effected by the well-known chemical reaction with ferrocyanides, the production of the precipitate of Prussian blue. Although it has been impossible to devise an analytical process for the separation of iron and alumina by the application of this reaction, the reason of the failure having been that the blue precipitate obstinately refuses to fall out of the solution, the author was successful in contriving a means of using it for the purification of aluminous solutions, which involves a curious physical change in the character of the blue precipitate not before observed. It was found that the addition of only a trace of copper, or even of zinc salt, to the aluminous solution, free from any excess of ferrocyanide, caused an aggregation of the particles of the imponderable blue precipitate, and so altered its physical condition that it separated perfectly from the liquid, leaving it clear and colourless.

In conclusion the author gives a short description of the actual process of manufacture as carried on at the St. Helen's Chemical Works, where 25 tons of pure aluminium sulphate are turned out weekly by the application of the above process, and it is contemplated to increase the production to double this quantity. D. B.

Examination of the Raw Materials used for Arita Porcelain.

By NAWOKICHI MATSUI (*Chem. News*, **42**, 207).—The samples examined came from Koransha, a large porcelain manufacturing company of Arita, in the province of Hizen, Japan. The native minerals used in the manufacture are all white, varying considerably in hardness, and apparently showing different stages of decomposition of feldspathic rocks. The larger part of this paper is occupied with the results of the analyses of the sixteen different materials used in the manufacture, and also with the results of determination of sp. gr. and fusibility. D. B.

Note on Siemens-Martin Steel. By S. KERN (*Chem. News*, **42**, 287).—This steel is in most cases used for ship-building and boiler-making. The author has noticed that its ingots stand heat better, and roll more softly than Bessemer ingots containing the same quantity of carbon. Moreover, they contain, as a rule, less manganese than Bessemer ingots, and, as plates containing much manganese are more liable to oxidise, the Siemens-Martin plates are preferable for the above-mentioned purposes. The author has drawn up a table which shows that Siemens-Martin steel, giving a high elongation, stands a good breaking strain, taking into consideration the percentage of carbon (0.45 to 0.60 per cent.) Bessemer steel containing the same amount of carbon never gives such good results. D. B.

Metallurgic Treatment of Complex Ores containing Zinc.

By E. A. PARNELL (*Chem. News*, **42**, 201).—It is well known that the presence of zinc in considerable quantity in ores containing other metals has a very injurious influence on the ordinary smelting processes for the extraction of the latter. In the case of copper ores, *e.g.*, the presence of much zinc necessitates additional operations in order to obtain copper of good quality; and all the zinc originally present in the ore is lost. The extraction of zinc from such ores in a useful form has often been attempted by means of hydrochloric acid, after calcination of the ore, with a view of decomposing the chloride of zinc by lime. Serious impediments, however, to this method have prevented it from being adopted, especially the difficulty of washing the oxide of zinc from the chloride of calcium and obtaining it in a dense form suitable for the spelter manufacturer; also the injurious influence of the presence of chlorine in any form in the subsequent smelting of the residue containing lead and silver. The separation of oxide of zinc from the calcined ore can of course be easily effected by sulphuric acid, but the great objection to this method has been the difficulty of obtaining oxide of zinc from the sulphate in a form suitable for the spelter manufacturer. The author has devised a process which is worked on an extensive scale, and completely overcomes this difficulty. When heated alone, sulphate of zinc requires a very high temperature to effect decomposition. Such a method is impracticable on the large scale, but when mixed with a small proportion of deoxidising agent, sufficient to take one equivalent of oxygen from the sulphate, it is easily decomposed with the production of oxide of zinc and sulphurous acid. A mixture of 2 equivalents of sulphate of zinc with 1 equivalent of carbon, heated to dull redness, affords oxide of zinc. With a larger proportion of carbon, sulphide of zinc is produced. 3 equivalents of sulphate and 1 equivalent of sulphide produce 4 equivalents of oxide and 4 equivalents of sulphurous acid, thus: $3\text{ZnSO}_4 + \text{ZnS} = 4\text{ZnO} + 4\text{SO}_2$. Native sulphide of zinc is the reducing agent, which the author prefers on the large scale for making oxide of zinc suitable for the zinc manufacturer. For the further treatment of the portion of the ore left undissolved, the ordinary smelting processes are resorted to, the products being argentiferous and auriferous lead and also copper regulus, which generally contains both gold and silver. The following ores have been operated on:—

1. Complex ore from Cavalo (Algeria), containing, as sulphides, Zn, 17 per cent.; Pb, 16 per cent.; Ag, 20 oz. per ton.
2. Cupriferous blende from Ain Barbar (Algeria), containing Zn, 23 per cent.; Cu, 6 per cent.; Ag, 6 oz. per ton.
3. Complex ore from Italy, containing Zn, 20 per cent.; Pb, 12 per cent.; Cu, 5 per cent.; also silver.
4. "Bluestone" from Anglesea, containing Zn, 28 per cent.; Pb, 12 per cent.; Ag, 12 oz. per ton; also Au and Cu.
5. Ore from Constantine (Algeria), containing Zn, 12 per cent.; Pb, 5 per cent.; Cu, 1.5 per cent.; Ag, 12 oz. per ton; also Au.

D. B.

General and Physical Chemistry.

Spectrum of Iron in the Sun. By J. N. LOCKYER (*Compt. rend.*, **92**, 904—910).—The author has carefully studied the lines in various iron spectra in the region between D and F. The lines in the spectrum of metallic iron in the voltaic arc closely resemble the lines due to the same metal in the solar spectrum, but considerable differences are observed when a large induction coil arranged for intensity is used instead of the arc. The number of lines is then much reduced, and in many cases their relative intensities are reversed. In the spectra of sun-spots, large or small, the number of thickened lines is not great: not more than 10 per cent. of the lines known to be produced when metallic iron is volatilised are distinctly changed. A large number of the lines which are thickened in the sun-spots are visible in the spectrum of the vapour of iron produced by the oxyhydrogen blow-pipe. The vapours which produce the lines in the spectra of sun-spots must be highly complex, for these lines cannot be arranged in a continuous series, as would be the case if they were due to successive dissociations of similar molecules. Further, the spectra of sun-spots and protuberances have not a single iron line common to both. The lines observed by Tacchini in the spectra of protuberances are, as a rule, lines which are the most brilliant in the iron spectrum given by the most powerful induction coil. These lines are present in the spectra of substances other than iron, even when the lines characteristic of the latter at the particular temperature are absolutely invisible. Moreover, the distortion of the lines, indicating rapid movement of the vapours which produce them, is not always of the same character. Different lines indicate different movements, and in the rapidity of the movements thus indicated inversions are observed similar to those in the relative intensity of the different lines.

From these observations the author concludes that iron does not exist, as such, in the nucleus of the sun, but is dissociated into its constituents. These constituents exist at different levels in the sun's atmosphere, and by their condensation produce forms of the most complex character. A drawing of a portion of the spectrum of iron under different conditions accompanies the paper. C. H. B.

Intensity of the Luminous Radiation from Incandescent Platinum. By J. VIOLLE (*Compt. rend.*, **92**, 866—868).—The author has determined the intensity of the luminous radiations of different wave-length, from incandescent platinum at the following temperatures: 755°, 954°, m. p. of silver; 1045°, m. p. of gold*; 1500°, m. p. of palladium; and 1775°, m. p. of platinum. His results may be expressed by the formula—

$$I = mT^3 (1 + ea^{-T}),$$

* In a previous paper (this Journal, 1880, Abstr., 149) this melting point was erroneously given as 1035°.

salt in light has very little to do with the energy with which the components are bound together, but is closely connected with the absorption, which also appears to be different in different parts of the spectrum.

Comparative experiments with ferric chloride and oxalic acid, and with mercuric chloride and oxalic acid, show that the iron mixture is much more rapidly decomposed than the mercury mixture.

For certain photographic purposes, the author recommends the use of sodioferric oxalate, which is beautifully crystalline, very sensitive to light, and soluble in water. W. R. H.

Faure's Secondary Electric Pile. By E. REYNIER (*Compt. rend.*, **92**, 951—952).—The pile devised by Faure does not differ essentially from that of Planté. The latter employs electrodes of sheet lead, whilst the former obtains a greater amount of force by employing lead in a spongy form. The pile is prepared in the following manner. The two pieces of lead are covered with a layer of minium or another insoluble lead oxide, and firmly rivetted together with a layer of felt between. They are placed in this position side by side in the acidulated solution. If they be of great length they are rolled into a spiral. On passing an electric current through the pile, the minium on the positive electrode is converted into peroxide, and that on the negative into metallic lead. The pile is then charged. In discharging it, the lead oxidises, and the peroxide reduces. In this manner an amount of energy equal to one horse-power for an hour can be stored up in a pile weighing 75 kilos. The yield of power is about 80 per cent. of the charge. J. I. W.

Electric Conductivity of Heated Gases. By R. BLONDLOT (*Compt. rend.*, **92**, 870—872).—Becquerel stated that gases when heated to redness conduct voltaic electricity, but this has been doubted by subsequent observers. The author connected the extremities of a circuit containing a copper sulphate element and a capillary electrometer, with two similar pieces of platinum foil, placed parallel with each other at a distance of 2 to 3 mm. When the platinum plates were heated to redness, and consequently the layer of air between them heated, a very distinct movement of the mercury in the electrometer was observed. With five Bunsen cells in the circuit, the current was conducted by the layer of air when heated only to 60—70°. The interposition of a screen, or agitation of the air, interfered with the conduction.

If the two plates of platinum are unequally heated, considerable electromotive force is developed, the hotter plate being negative with respect to the other, a phenomenon similar in kind to that observed in a flame by A. Becquerel. C. H. B.

Changes of Volume Accompanying Electrolytic Deposition of a Metal. By E. BOURY (*Compt. rend.*, **92**, 868—870).—The pressure exerted on an electrode by an electrolytically deposited film of metal, and the Peltier effect observed at the point of contact of an electrode and an electrolyte are connected one with the other: the

former is a consequence of the latter. The Peltier effect is readily detected when the electrolysis is not complicated by energetic secondary actions, and is especially well marked with copper sulphate and nitrate, and the sulphates and chlorides of cadmium and zinc. For any of these salts an intensity of current, I , can be determined such that for all higher intensities the electrode is heated, for all lower intensities it is cooled. This particular intensity may be called the *point of neutral temperature*. In the electrolysis of the same salts, it is also possible to diminish the intensity of the current below a point, I' , such that the metallic deposit, instead of contracting at the moment of solidification, expands. This may be called the *point of neutral pressure*. In the electrolysis of salts of iron, nickel, &c., no point of neutral temperature or neutral pressure is observed: the negative electrode is always heated and the deposit always exerts a pressure on the electrode. The author has determined the constants in the formula given in a previous paper (this Journal, 1879; Abstr., 576; *Compt. rend.*, 88, 714—716), which gives the apparent excess, y , of the thermometer electrode compressed by the deposited metal, in terms of the time in which the metal has been deposited—

$$y = \frac{At}{B + t}.$$

The constant A is proportional to the variation in volume of a unit volume of metal; its value may, within practical limits, be represented by the formula—

$$A = -a'i + b'i^2,$$

an expression similar to that for the heating effect on the thermometer electrode—

$$E = -ai + bi^2.$$

Moreover, all causes, such as dilution of the liquid, the nature of the acid in the salt, &c., which cause a or b to vary, affect a' and b' in the same manner. The close relationship between the thermal and mechanical effects observed at the negative electrode is evident. The thermometer indicates the mean temperature of the liquid immediately surrounding its bulb, and this temperature is not necessarily that of the deposited metal. The current does not directly affect the temperature of the solvent, the molecules of which exchange heat with the molecules of the electrolyte: when a heating effect is observed, the latter will usually have a higher temperature than the former; when a cooling effect is observed, they will usually have a lower temperature. In the first case the metal at the moment of deposition is hotter than the liquid, and therefore than the thermometer; immediately after deposition it is cooled, consequently contracts, and exerts pressure. In the second case the metal immediately after deposition is heated, and therefore expands.

It is found, however, that sometimes the deposited metal expands, although the thermometer rises; sometimes it contracts, although the thermometer falls: but it must be borne in mind that the thickness of the molecular layer in which the heat is developed is infinitely small compared with the thickness of the layer, the temperature of which is

indicated by the thermometer. It is therefore not surprising that the two variations of temperature do not follow the same law.

C. H. B.

Chloride, Bromide, and Iodide of Sulphur. By J. OGIER (*Compt. rend.*, **92**, 922—924).—The author has determined the heat of formation of the haloid compounds of sulphur from their elements by direct synthesis, with the following results, calculated for solid sulphur:—

	Solid compound. cals.	Liquid compound. cals.	Gaseous compound. cals.
$S_2 + Cl_2$, gas.....	—	+ 17·6	+ 11·0
$S_2 + Br_2$, gas.....	—	+ 10·0	—
$S_2 + Br_2$, liquid	—	+ 2·0	—
$S_2 + Br_2$, solid	—	+ 0·9	—
$S_2 + I_2$, gas	+ 10·8	—	—
$S_2 + I_2$, liquid	+ 0·0	—	—

The further action of chlorine and bromine on the compounds S_2Cl_2 and S_2Br_2 respectively, at ordinary temperatures, is accompanied by a very slight development of heat, showing that if higher chlorides or bromides exist, they are very readily dissociated. The specific heat of sulphur chloride, S_2Cl_2 , between $+70^\circ$ and $+12^\circ$ is $0\cdot220$ (Regnault, $0\cdot204$ between 20° and 5°); its heat of vaporisation is $6\cdot665$ cal.

The formation of gaseous sulphur chloride from gaseous sulphur and chlorine develops heat = $+32\cdot4$ cal. ($S_2Cl_2 = 135$). C. H. B.

Heat of Formation of Sulphur Oxides. By BERTHELOT (*Ann. Chem. Phys.* [5], **22**, 422—429).—Numbers previously given for the heat of formation of sulphurous anhydride have been more or less inaccurate, since no corrections have been made for the formation, in addition to the sulphurous anhydride, of other oxides of sulphur in quantities depending on the rapidity and temperature of the combustion, and of sulphuric acid owing to the presence of moisture. When sulphur is burned in air or oxygen, sulphuric anhydride is formed in relatively large quantities, and the greater part remains in the gaseous condition, owing to its high vapour-tension ($0\cdot177$ mm. at 18°). In a long series of experiments, the author has carefully estimated the relative proportions of sulphurous and sulphuric anhydrides formed, and finds that when all necessary corrections are made, the heat of formation of sulphurous anhydride, SO_2 (64 grams), is $69\cdot26$ cal., a number which holds good for octohedral, prismatic, and insoluble sulphur, with addition in the case of prismatic sulphur, of $0\cdot08$ cal. for 32 grams.

C. H. B.

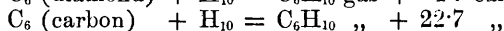
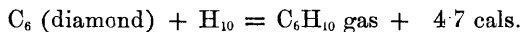
Vapour of Ammonium Dihydrosulphide. By ISAMBERT (*Compt. rend.*, **92**, 919—922).—The tension of the vapour of pure dry ammonium dihydrosulphide at different temperatures is given in the following table:—

t° .	Tension of vapour. mm.	t° .	Tension of vapour. mm.	t° .	Tension of vapour. mm.
4.2	132	18.0	322	33.2	804
6.1	142	22.0	410	35.6	919
7.9	159	25.1	501	37.9	1062
9.5	175	28.0	588	39.3	1156
10.1	184	30.9	696	42.0	1353
12.0	212	32.1	748	44.4	1560
15.0	259	32.6	772		

The curve representing the dissociation of the dihydrosulphide closely resembles, and from 25° almost coincides with, that representing the dissociation of ammoniacal calcium chloride. In presence of a gas such as hydrogen or nitrogen, the maximum tensions have the same values, the total pressure being the sum of the pressures of the gas and the hydrosulphide. In presence of hydrogen sulphide or ammonia gas, however, the total pressure is distinctly lower than the sum of the pressure of the free gas and the maximum tension of the vapour of the hydrosulphide. Direct experiment shows that this effect is not due to any absorption of the free gas, proving that the dihydrosulphide is less volatile in presence of its elements than in a vacuum or in presence of an inert gas such as hydrogen. In presence of ammonia or hydrogen sulphide, the maximum tension of the dihydrosulphide at a given temperature diminishes rapidly as the tension of the free gas increases, and *vice versâ*. The compound formed by the union of carbonic anhydride and ammonia behaves in a similar way.

C. H. B.

Heat of Formation of Diallyl, Chlorinated Compounds, and Aldehyde. By BERTHELOT and J. OGIER (*Compt. rend.*, **92**, 769—774).—*Diallyl*.—Heat of combustion as determined by the method of explosion = + 902.3 cal. at constant volume; + 904.3 cal. at constant pressure, from which the heat of formation is found to be:—

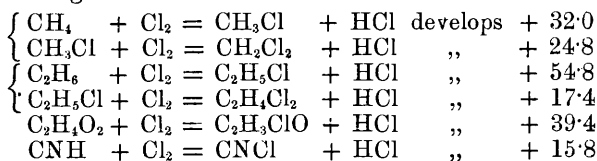


The formation of diallyl from dipropargyl, C_6H_6 gas, + $2\text{H}_2 = \text{C}_6\text{H}_{10}$, gas, develops heat = + 87.5 cal., a quantity much greater than that developed by the hydrogenation of any other known hydrocarbon, and nearly equal to that developed by the combination of oxygen and hydrogen. The production of diallyl from propylene develops + 41.3 cal.; that of dipropargyl from allylene develops + 10.2 cal. It is evident that changes in the hydrocarbon series, effected in accordance with similar equations, do not necessarily give rise to the same thermal phenomena, any more than in the series of metallic or non-metallic elements.

Methylene chloride, CH_2Cl_2 .—Specific heat between 40° and $15^{\circ} = 0.288$; molecular heat, 23.2; heat of vaporisation, 6.40. When it was exploded with oxygen, chlorine was set free. This is often observed in the combustion of chlorinated organic compounds, but the amount of chlorine liberated is less the greater the proportion of hydrogen in the

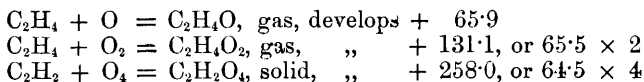
compound. After introducing the necessary corrections for the chlorine thus set free, the heat of formation of methylene chloride, $C(\text{diamond}) + H_2 + Cl_2 = CH_2Cl_2$, gas = + 31.2 cal.; liquid = + 37.6 cal. The combination $C + 2HCl$ would absorb - 12.8 cal.

Ethylidene chloride, $C_2H_4Cl_2$, prepared from paraldehyde.—Specific heat between 50° and $13^\circ = 0.315$; molecular heat, 31.2; heat of vaporisation, 6.63; heat of formation, C_2 , diamond, + $H_4 + Cl_2 = C_2H_4Cl_2$, gas = + 33.9; liquid = + 40.5. Its formation from acetylene, $C_2H_2 + 2HCl = C_2H_4Cl_2$, gas, would develop + 29.0×2 cal., a number very near the heat of formation of ethyl chloride from ethylene (+ 31.9). The heat of combustion of ethylidene chloride at constant volume = + 267.4 cal.; at constant pressure = + 267.1 cal. The heat of combustion of methylene chloride at constant volume = + 107.3 cal.; at constant pressure + 106.8 cal. A comparison of the following reactions—



shows that the heat developed by the substitution of chlorine for hydrogen in organic compounds decreases as the number of atoms substituted increases, and also varies with the series and chemical function.

Aldehyde. — Heat of formation; gas = + 50.5 cal.; liquid, + 56.5 cal.; dissolved, + 60.1 cal. The heat of formation of acetic acid is therefore: gas, + 119.7 cal.; liquid, + 126.6 cal.; solid, + 129.1 cal.; dissolved, + 126.9 cal.; and its heat of combustion is + 199.4. Favre and Silbermann found 210.3. The oxidation of ethylene and acetylene gives the following results:—



Methylal.—Specific heat between 41° and $15^\circ = 0.521$; molecular heat, + 39.6; heat of solution in 75 parts of water at 11° , + 3.2; heat of vaporisation, 6.83. Heat of formation from its elements, gas = + 117.3; liquid, + 124.1 cal. Its production from methyl alcohol, $3CH_3O + O = C_3H_8O_2 + 2H_2O$, develops + 76.1 cal., a quantity somewhat greater than that developed by the formation of aldehyde from ethyl alcohol (+ 70.1). The heats of formation and combustion of methylal are nearly the same as those of the two propylenic glycols, as determined by Longuinine, the heat of combustion of methylal being + 433.9, that of propylenic glycol, + 431.2; and that of iso-propylenic glycol, + 436.2. C. H. B.

Chloral Alcoholate. By BERTHELOT (*Compt. rend.*, 92, 826—831).—The solution of crystalline chloral alcoholate in twenty-five times its own weight of water at 14° produces no sensible thermal effect, and

no rise of temperature is observed when aqueous solutions of chloral and alcohol are mixed in equivalent proportions. From this it is evident that the heat of combination of pure chloral and alcohol is equal to the sum of the heats of solution of these two bodies, taken separately, in the same quantity of water. The heat of formation of solid chloral alcoholate at $14^{\circ} = +14.4$ cal.; that of chloral hydrate at the same temperature being 12.1 cal. It follows therefore that alcohol, when brought in contact with chloral hydrate, will displace the water, forming the alcoholate, a fact which Personne has previously observed and utilised as a means of preparing the latter compound. In presence of a large excess of water, however, this action is reversed. Crystals of the alcoholate, when thrown into a large quantity of water, become white and opaque, being converted into the hydrate. The alcoholate, even at ordinary temperatures, contains a certain proportion of free chloral and alcohol, which, with the alcoholate, form a system in equilibrium. In presence of water, the free chloral forms the solid hydrate, which remains mixed with crystals of the alcoholate, whilst the free alcohol is diffused through the water. The alcohol and chloral being thus removed, the equilibrium of the system is destroyed; further quantities of alcohol and chloral are set free; these are again removed, and this series of changes goes on until the alcoholate is entirely converted into hydrate. This decomposition is accompanied by a slight development of heat, the heat of formation of the solid chloral hydrate and the heat of solution of the alcohol being together somewhat greater than the heat absorbed in the decomposition of the chloral alcoholate. The rise of temperature is, however, only temporary, since solution of the chloral hydrate soon brings the liquid to its original temperature.

The specific heat of solid chloral alcoholate between 46° and 14° , and its heat of fusion, are not constant, and cannot be determined with accuracy, owing to the dissociation of the compound into alcohol and chloral. Assuming, according to Kopp's theory, that the true specific heat is 0.244 , the heat of fusion is $+4.65$ cal., a value somewhat near that for the hydrate, $+5.2$ cal. The heats of formation of chloral alcoholate and hydrate at different temperatures and in different states, are given in the following table:—

	Chloral alcoholate. cals.	Chloral hydrate. cals.
Solid, at 14°	+ 14.4	+ 12.1
Liquid, about 50° (near the melting point) ..	+ 9.8	+ 7.3
Liquid, near the boiling point	+ 8.5	+ 6.2
Gaseous (from gaseous constituents)	+ 1.6	+ 2.0

C. H. B.

Liquefaction of Gaseous Mixtures. By L. CAILLETET and P. HAUTEFEUILLE (*Compt. rend.*, **92**, 901—904).—The complete liquefaction of a mixture of an easily liquefiable and a so-called permanent gas may be effected by subjecting the gaseous mixture to great pressure at a temperature sufficiently high to prevent liquefaction, and then lowering the temperature so regularly that all parts of the capillary tube containing the gases reach the temperature at which a

change of state takes place at the same time. In this way, liquefied carbonic anhydride can be obtained containing large proportions of liquid oxygen, nitrogen, and hydrogen. The authors have also studied the behaviour of mixtures of more readily liquefiable gases at temperatures at which the least easily liquefiable would remain gaseous if pure. Of such mixtures, that of carbonic anhydride and cyanogen may be taken as the type. If the carbonic anhydride is present in largest proportion, a contraction of $\frac{1}{100}$ of the volume at 0° is observed: if the cyanogen preponderates, there is a contraction of $\frac{3}{1000}$. The following table gives the density of the liquid carbonic anhydride in the mixture under different pressures, compared with the density which it would have if pure at 33° , if it could exist in the liquid state at that temperature:—

Pressure.	Temperature.	Density of liquid CO ₂ .	Density of liquid CO ₂ in the mixture.	Diminution of density for 1° .
100 atmos. . .	{ -23	1.092	1.046	—
	{ 0	0.984	0.991	0.0023
	{ 30	"	0.893	0.0032
	{ 33	"	0.883	0.0033
150 " . .	{ -23	1.111	1.073	—
	{ 0	0.015	1.010	0.0028
	{ 30	"	0.918	0.0030
	{ 33	"	0.907	0.0030
0.2 " . .	{ -23	1.126	1.095	—
	{ 0	1.039	1.033	0.0027
	{ 30	"	0.940	0.0031
	{ 33	"	0.931	0.0030

The carbonic anhydride must probably be regarded as liquid dissolved in the liquefied cyanogen. Experiments have been made to determine the density of liquid oxygen, hydrogen, and nitrogen in mixtures of this character. C. H. B.

Changes of State near the Critical Temperature. By L. CAILLETET and P. HAUTEFEUILLE (*Compt. rend.*, **92**, 840—843).—One drop of blue oil of galbanum was dissolved in liquid carbonic anhydride in the glass tube of a Cailletet's apparatus. Any total or partial change of state could thus be easily followed; for as the liquid passed into the gaseous state, it left the colouring-matter on the surface of the mercury and the sides of the tube. By this means it was proved that above 31° the carbonic anhydride is entirely in the gaseous condition; the striæ which make their appearance just at the critical point being due to a partial condensation of the gas to the liquid state. It was also proved that the disappearance of the meniscus or line of separation, observed when a mixture of a gas and a vapour already partially liquefied is subjected to increased pressure, is due to the revolatilisation of the liquid, the tube being entirely filled with gas, which shows signs of liquefaction when either the temperature or pressure is lowered. C. H. B.

Evaporation without Fusion. By L. MEYER (*Ber.*, 14, 718—723).—The author gives an account of some experiments made in order to ascertain whether in the experiment described by Carnelley (*Proc. Roy. Soc.*, 6th January, 1881) the ice has a temperature higher than that of its melting point. From these experiments, it would appear that the temperature of the ice does not rise above its melting point, but varies with the temperature of the freezing mixture used to condense the aqueous vapour. In one case, the temperature indicated by the thermometer was 20° , this being due to a portion of the bulb becoming bare, and consequently exposed to radiation; and in this case, when the pressure was increased in the apparatus by admitting air, the ice melted slowly, and not quickly, as would have been the case if its temperature had been higher than its melting point.

P. P. B.

Viscosity of Gases. By W. CROOKES (*Compt. rend.*, 92, 862—866).—Some time ago Maxwell showed that the coefficient of friction or viscosity of a gas should be independent of its density, and this conclusion is verified by experiment for pressures between 762 mm. and 13 mm. This law assumes, however, that the mean free path of the molecules is very small compared with the size of the vessel containing the gas, and it appeared probable that at high degrees of exhaustion, when the free path is much greater, this law would not hold good. With the Sprengel pump, it is easy to obtain a vacuum in which the mean free path of the gaseous molecules may be measured in centimeters or even meters. Assuming that at the pressure of 1 atmosphere the mean free path is 0.0001 mm., at 0.0001 atmosphere, it will be 1 mm., at 0.000001 atmosphere, 10 cm., and at 0.00000001 atmosphere, 10 meters. The latter pressure corresponds approximately with a height of 144 kilom. above the earth's surface; at greater heights the free path will be comparable with planetary distances. At about 450 kilom. for example, it would be equal to the distance between the earth and Sirius. The author has determined the viscosity of different gases at exhaustions down to 0.02 millionth of an atmosphere, by observing the oscillations of a mica disc suspended by means of a fine glass thread in the vessel containing the gas to be experimented with. His results are given, together with those of other observers, in the following table:—

	Graham.	Kundt and Warburg.	Maxwell.	Crookes.
Air.....	1.0000	1.0000	1.0000	1.0000
Oxygen.....	1.1099	„	„	1.1185
Nitrogen.....	0.971	„	„	0.9715
Carbonic anhydride	0.807	0.806	0.859	0.9208
Carbonic oxide....	0.971	„	„	0.9715
Hydrogen.....	0.4855	0.488	0.5156	0.4439

Hydrogen is distinguished from all other gases by the fact that its viscosity remains the same for all pressures between 760 mm. and a thousandth of an atmosphere. The ratio between air, oxygen, nitrogen, and carbonic oxide is practically the same under all pressures; whilst the ratio between air and carbonic anhydride is constant between 760 mm. and 650 mm., then decreases as the pressure diminishes to

about 50—55 mm., at which point it again becomes constant. The effect of pressure in increasing the viscosity of a gas is greater the more easily the gas is liquefied. It is least with hydrogen, somewhat greater with oxygen and nitrogen; whilst the viscosity of carbonic anhydride, which liquefies under a pressure of 56 atmospheres at 15°, increases rapidly.

Maxwell's law is true within certain limits, beyond which it does not hold good. For hydrogen it is true between 0.760 and 0.001; for carbonic anhydride, carbonic oxide, oxygen, nitrogen, and air, it only holds good between 0.015 and 0.035. The passage into the ultra-gaseous condition begins at 0.0005. It is slow with hydrogen, but more rapid with the less perfect gases. In ordinary gases differences of pressure on the sides of the containing vessel are rapidly equalised, electrified bodies lose their electricity, and the rate of cooling of a heated body is not sensibly affected by variations in pressure such as may be obtained with an ordinary air-pump, the difference in the velocity of the molecules before and after encounter compensating for the decrease in their number. In the ultra-gaseous condition differences of pressure can exist for twenty minutes; electrified bodies retain their electricity for so long a period as thirteen months, and at high exhaustions the rate of cooling of a heated body is considerably diminished. The ordinary gaseous condition is retained so long as the number of molecular encounters may be regarded as almost infinite. When, however, the number of encounters in a given time becomes so small as to be negligible, and the mean free path of a molecule becomes comparable with the dimensions of the containing vessel, the substance has passed into the ultra-gaseous state.

C. H. B.

Quantivalence of Carbon. By A. CLAUS (*Ber.*, 14, 432—435).—The author argues against the notion that the atom of carbon contains four distinct points of attraction.

W. C. W.

The So-called Differences in the Quantivalence of a Multivalent Atom. By W. LOSSEN (*Ber.*, 14, 760—765).—This consists essentially of a criticism of the views of Claus (*Ber.*, 14, 432). Attention is also directed in the author's publication on a closely allied question (*Annalen*, 204, 272), viz., on the combination of atoms, in which the theory of valency is not used, as the author thinks the present form of this theory should be rejected.

P. P. B.

Magnitudes of Affinity in Carbon. By H. KLINGER (*Ber.*, 14, 783—785).—The author criticises Claus' remarks on this subject (*Ber.*, 14, 432), and draws attention to Kommrath's treatment of the same subject (*ibid.*, 9, 1094, and 10, 742). With regard to the limited divisibility of the force of attraction of atoms, the author thinks our present position may be illustrated by the following example:—A magnet whose load is 10 kilos. can carry any number of pieces of iron, provided that their total weight is not more than 10 kilos., and the divisibility of its power would appear unlimited. If, however, we have pieces of iron weighing 5 and 2 kilos. only, then it would appear as though the magnet's power could be divided into 2 and 5 parts

only. If the force of attraction of atoms obeys Newton's law of equality of action and reaction, supposing the value of the affinity of univalent atoms or groups to be expressed as lying between 80 and 90, that of bivalent atoms will be between 160—170 such units. Then an atom with the power 170 can combine with two atoms of 80 or 90, and so form groups each possessing 10 free units of power, which may show their influence by giving rise to molecular compounds, &c.

P. P. B.

Measure made of a 10 Per Cent. Iridium Platinum Alloy. By O. J. BROCH, H. ST. CLAIRE-DEVILLE, and J. STAS (*Ann. Chem. Phys.* [5], 22, 120—144).—This paper is a description of the preparation of the iridio-platinum standard measure for the Comité International des Poids et Mesures (cf. Matthey, this Journal, 1879, Abstr., 772—774).—*Platinum*.—Two samples of platinum prepared by Matthey gave on analysis by the authors:—

	Sample A.	Sample B.
Platinum	99·892	99·890
Rhodium	0·065	0·070
Iridium	0·029	0·023
Loss	0·014	0·017
	<hr/> 100·000	<hr/> 100·000

Iridium.—The sample of iridium, owing to difficulties which arose in preparation, still contained a considerable proportion of platinum; but this presents no inconvenience so far as regards the preparation of the alloy is concerned. The iridium gave on analysis:—

Iridium.....	91·100
Platinum	8·480
Rhodium	0·122
Ruthenium	0·120
Iron	0·042
Loss	0·136
	<hr/> 100·000

Iridio-platinum Alloy.—The sample of platinum A was mixed with the platiniferous iridium in such a proportion as to contain 10·25 per cent. pure iridium, the slight excess being added to compensate for the loss of iridium by oxidation during the preparation of the alloy. The mixture was then repeatedly passed through a very fine silk mesh, the operation being performed in a closed vessel. The powder was fused, allowed to cool slowly, cleaned with dilute hydrochloric acid, and forged. The ingot obtained was then passed through steel rolls, cleaned with red-hot potassium pyrosulphate, and then with 1·10 boiling hydrochloric acid. In order to obtain a perfectly homogeneous alloy, these operations were repeated three times.

Samples were detached before the definite forging of the ingot, which was effected with the necessary precautions of avoiding the

action and penetration of iron. One of the ends of the bar obtained was detached for analysis. For the final forging, the bar was introduced into a thick platinum tube, enclosed in a second tube of refractory clay, heated to a white heat in a furnace filled with heavy coal-tar oil, to avoid contamination with particles of oxide of iron. The bar was then planed and shaped in the form of an X, an operation which required 448 hours. The shavings detached during this process were analysed:—

Specific gravity of the alloy after the first forging..	21·535
" " " a definite forging	21·543
" after a series of blows.....	21·553

Composition of the Alloy of the Standard (detached shavings).

Iridium	10.1496
Iron	0.0420
Ruthenium.....	0.0180
Rhodium.....	0.0380
Platinum.....	89.6300
Loss.....	0.1224

100.0000

Following the advice of one of the authors, Matthey *drew* parts of the standard rule through steel plates; but after the operation, there were found on the surface a series of longitudinal lines of a bluish-black colour in the direction of the *draw*. It was found that these lines were due to ferrosoferric oxide, and the alloy contained a larger percentage of iron than that fixed upon by the Comité. It was necessary to recommence the purification of the alloy, and to shape the X rule entirely by *planing*, and not by *drawing*.

As the Comité International had decided that the alloy for the standard meter and standard kilogram should be cast in a single cylinder, Matthéy made three successive castings; two with the sample A, one with the sample B of platinum, the iridium described above being used in both cases. The second casting had a sp. gr. 21.553; the third a sp. gr. 21.5529; the latter gave on analysis*:

	Per cent.
Iridium	10·127
Iron	0·098
Ruthenium	0·0098
Rhodium	0·0500
Platinum	89·753

The percentage quantities of the metals in the second casting were practically the same; thus showing, contrary to the original opinions of the authors, that it is possible to obtain an identical composition even with separate castings and materials. The rule of the X form has been finished by Brunner, and is now laid before the Comité International.

V. H. V.

* Mean of two independent analyses.

Inorganic Chemistry.

Attempts to Prepare Boron Oxytrichloride. By A. MICHAELIS and P. BECKER (*Ber.*, **14**, 914—915).—Boron oxytrichloride is not formed either by passing electric sparks through a mixture of oxygen and boron trichloride vapour, or by the action of ozone on boron trichloride.
W. C. W.

Preparation of Adamantine Carbon or Diamond. By R. S. MARSDEN (*Proc. Roy. Soc. Edin.*, **11**, 20—27).—On heating to a high temperature for 10 hours, and then cooling very slowly, a mixture of silver and amorphous carbon (from sugar), three forms of carbon are found to exist in the silver, from which they can be readily removed by treating the mass with nitric acid: the three forms are: graphite, in largest proportion; a number of small crystalline bodies of octohedral form, and a quantity of a brownish substance, probably amorphous carbon, or silver carbide. This last form, which is flocculent, is easily removed by washing the mixture of carbon with hydrofluoric acid, ammonia, and potash: the crystals thus cleaved are hard, scratching quartz, glass, and sapphire, and burn away slowly when heated in a stream of oxygen.

Microscopic examination of the crystals shows that there are two kinds present, dark coloured, and transparent. The dark coloured ones are believed to be true diamonds, the darkness being due to dissemination of amorphous carbon through them; they have a perfect octohedral form with curved edges.

The transparent crystals have an adamantine lustre, and high refractive power; this form is octohedral, but the edges are not curved, and they act on polarised light.

The author believes that by employing 200—300 oz. of metal, he will be able to produce larger diamonds, fit for rock-boring.

E. W. P.

Sodium Hyposulphite. By P. SCHUTZENBERGER (*Compt. rend.*, **92**, 875—878).—The author maintains that the true formula of sodium hyposulphite is NaHSO_2 . The compound $\text{Na}_2\text{S}_2\text{O}_4$ obtained by Berntsen is probably a product intermediate between the bisulphite and the hyposulphite, a supposition which is supported by Berthelot's observation that the development of heat by the oxidation of the hyposulphite takes place in two distinct stages.
C. H. B.

Some Properties of Ammonium Bromide. By J. M. EDER (*Wien. Akad. Ber.*, **82**, 1284—1287).—The author has investigated some properties of pure ammonium bromide. Its sp. gr. in the crystalline state is 2.327, after sublimation, 2.3394. The salt is not altogether stable in presence of light and air; it turns a golden colour, and contains hydrobromic acid and free bromine.

The author found that a decrease of temperature is produced when

ammonium bromide is dissolved in water. The following are the values of the solubility for 1 part of the salt in water:—

10°.	16°.	30°.	50°.	100°.
1·51	1·39	1·23	1·06	0·78

One part ammonium bromide requires 32·2 parts of alcohol at 15°, and 890 parts of boiling alcohol. Aqueous ammonium bromide solution of various concentration showed the following specific gravities:—

Per cent. of ammonium bromide in solution	5	10	15	20
Specific gravity of solution at 15°..	1·0326	1·0652	1·096	1·1285

The dissociation of ammonium bromide solution begins at 16°, and is very marked at 30°. Quantitative experiments were made with a view of determining the amounts of ammonia obtained by the distillation of an ammonium bromide solution (3·100). The amounts of ammonia so given off decrease after each successive distillation, in proportion as the hydrobromic acid remaining in solution increases. An alcoholic solution of ammonium bromide evolves ammonia on boiling.

On heating dry ammonium bromide, which always shows an acid reaction, large quantities of ammonia are evolved at the commencement of the sublimation.

V. H. V.

Decomposition of Bicalcium Phosphate. By C. DELATTRE (*Bull. Soc. Chim.* [2], **35**, 358—360).—Bicalcium phosphate dried at 130° has the formula $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 + 4\text{H}_2\text{O}$, and at 150° it loses 1 mol. H_2O . By boiling a solution of bicalcium phosphate, it is completely decomposed into mono- and tri-calcium phosphates—



If, however, some undissolved bicalcium phosphate is present, on boiling two or three times, the solution, which at first becomes acid, afterwards becomes neutral owing to an equilibrium being formed, the reverse reaction taking place.*

L. T. O'S.

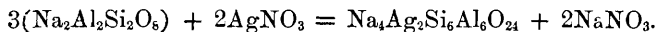
Crystalline Hydrated Barium Silicate. By LE CHATELIER (*Compt. rend.*, **92**, 931—932).—When kept for some time, solutions of baryta deposit a yellowish-white powder, and on the sides of the containing vessel beautiful transparent crystals are formed. These crystals, and apparently the deposit, have the composition $\text{BaSiO}_3 + 7\text{H}_2\text{O}$. They may be preserved unaltered for a considerable length of time in air or water at ordinary temperatures, but are decomposed by boiling water. The crystals, which are orthorhombic, lose their water at a little above 100°, and acquire a turquoise-blue colour. They may be easily obtained by suspending calcined silica in baryta-water. At the

* Millet has shown (this Journal, **38**, 422) that bicalcium phosphate can be completely converted into tricalcium phosphate by repeated boiling with fresh quantities of water. Moreover, when dried at 100° it has the formula $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 + 5\text{H}_2\text{O}$. —L. T. O'S.

end of some days, the sides of the vessel are covered with microscopic crystals, having the crystallographic characters of those previously described. Since these crystals are deposited on the sides as well as on the bottom of the vessel, the silica must have been dissolved by the baryta-water. No corresponding natural silicate is known.

C. H. B.

Sodio-aluminic Silicates formed by the Action of Sodium Carbonate on Kaolin. By P. G. SILBER (*Ber.*, **14**, 941—946).—A substance having the same percentage composition as nepheline, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_6$, is produced by heating kaolin and sodium carbonate in their molecular proportions, in an ultramarine furnace. It is insoluble in water, but is converted into a gelatinous mass by hydrochloric acid. By using two molecules of sodium carbonate to one of kaolin, a silicate having the composition $\text{Na}_4\text{Al}_2\text{Si}_2\text{O}_9$ is obtained. One-third of the sodium in the former of these compounds is converted into chloride by the action of hydrochloric acid. The same amount of sodium is also replaced by silver, when the silicate is heated in a sealed tube with a solution of silver nitrate. Hence it appears that the molecular formula must be at least three times greater than that usually ascribed to nepheline—



In the second silicate, three-fourths of the sodium is converted into chloride by the action of hydrochloric acid gas, and on treatment with silver nitrate, the sodium is completely replaced by silver, with formation of a yellow compound, $\text{Ag}_4\text{Al}_2\text{Si}_2\text{O}_9$. W. C. W.

Preparation and Properties of Chromous Chloride and Sulfate. By H. MOISSAN (*Compt. rend.*, **92**, 792—794).—*Chromous chloride*, CrCl_2 , may be obtained in the form of perfectly white crystals, mixed with particles of unattacked carbon, by the action of dry hydrochloric acid at a red heat on the regulus of chromium obtained by Deville's method. If chlorine is employed in place of hydrochloric acid, chromic chloride, Cr_2Cl_6 , is formed. White micaceous plates of chromous chloride, retaining the forms of the original chromic chloride, are obtained when vapours of ammonium chloride are passed over the latter, heated to a temperature approaching the softening point of glass.

In order to prepare chromous chloride in large quantity, a porcelain retort, the tubulus of which is fitted with a porcelain tube provided with a stopper, is half filled with dry chromic chloride mixed with a little ammonium chloride, and heated to redness. Fragments of ammonium chloride are from time to time dropped down the porcelain tube, the stopper being removed for that purpose. The ammonium chloride is partially decomposed, and the chromic chloride is reduced. The undecomposed ammonium chloride condenses in the neck of the retort, which is placed in a slanting position, and hydrochloric acid passes off. On cooling, the fused mass of chromous chloride thus obtained crystallises in long opaque needles, which sometimes contain a little chromium sesquioxide. It dissolves in water out of contact

with air, forming a beautiful blue solution, the properties of which have been studied by Peligot.

Chromous sulphate, $\text{CrSO}_4 + 7\text{H}_2\text{O}$, may be obtained in beautiful blue crystals isomorphous with the corresponding sulphates of other bases, by dissolving chromous acetate in dilute sulphuric acid and cooling the solution.

Chromous acetate may be prepared by reducing a solution of chromic chloride by means of zinc and hydrochloric acid, and adding to the blue solution of chromous chloride thus obtained a concentrated solution of sodium acetate. The red precipitate of chromous acetate is washed by decantation. If the chromous acetate be treated with an excess of concentrated, instead of dilute, sulphuric acid, a white crystalline precipitate is obtained, which consists of chromous sulphate containing less than 7 mols. H_2O .

Chromous sulphate absorbs oxygen with great rapidity, and is a very powerful reducing agent. When left in contact with acetic acid for some time, it is converted into chromic sulphate, the acetic acid being reduced. Like ferrous sulphate, it readily absorbs nitric oxide, becoming brown in colour.

C. H. B.

Chromous Bromide, Iodide, and Oxalate. By H. MOISSAN (*Compt. rend.*, 92, 1051—1053).—*Chromous bromide* is prepared (1) by reducing chromium sesquibromide with hydrogen; (2) by acting with dry hydrobromic acid at high temperatures on chromium; (3) by passing the vapour of bromine, carried along by nitrogen, over cast chromium heated to redness.

It is a white substance which becomes yellow on melting. When exposed to moist air it absorbs water and oxygen with great evolution of heat. It has a styptic taste, like the corresponding ferrous salt. Its aqueous solution is blue, and readily dissolves the sesquibromide, iodide, and chloride. Chromous iodide also dissolves any of the haloid per-salts of chromium.

Chromous iodide is prepared in a similar manner to the bromide. It is a grey solid. It dissolves in water with a blue colour. By treating a dilute boiling solution of chromic acid with an excess of hydrobromic or hydriodic acid and reducing with zinc, chromous bromide or iodide is obtained in solution.

Chromous oxalate is prepared as follows:—A quantity of chromous acetate is mixed with sufficient oxalic acid to dissolve it, in a flask through which a current of carbonic anhydride is kept passing. The mixture is then boiled for 10—15 minutes. The acetic acid distils off with the steam, and a greenish powder separates out. This is washed with water and alcohol saturated with carbonic anhydride, and finally dried in a porous vessel filled with the same gas. It is a yellow crystalline powder resembling ferrous oxalate. On heating in a closed tube or in a current of hydrogen at 440° , it yields sesquioxide of chromium. Ferrous oxalate, on the contrary, gives ferrous oxide.

J. I. W.

Molecular Properties of Tin and Zinc. By C. RAMMELSBURG (*Chem. Centr.*, 1880, 507—512).—Tin may be obtained in three distinct modifications: (1) grey, sp. gr. 5.8; (2) quadratic crystals

sp. gr. 7.0; (3) fused, sp. gr. 7.3. The first modification is converted into the second by heating to a temperature below the melting point, and, under certain circumstances, into the third modification. The second modification is not changed by either heat or cold. The first modification is obtained by exposing the metal to low temperatures, as first observed by Fritzsche (*Ber.*, **2**, 112, 540).

The density of solidified zinc is not influenced, as Bolley (*Annalen*, **95**, 294) supposed, either by the mode of fusion or by that of cooling. The rapid conversion of the liquid into the solid metal increases the brittleness, and at the same time confers upon it a certain amount of passivity as regards the action of acids. T. C.

Uranates. By C. ZIMMERMANN (*Ber.*, **14**, 440—442).—*Potassium uranate*, K_2UO_7 , is obtained by evaporating a solution containing potassium, ammonium, and uranyl chlorides, to dryness and fusing the residue in a platinum crucible. On lixiviating the fused mass with water, the uranate remains as a lustrous orange-coloured powder, which dissolves easily in dilute acids. Sodium and lithium uranates, $Na_2U_2O_7$ and Li_2UO_4 , resemble the potassium salt in their properties. Lithium uranate, however, appears to be slowly decomposed by hot water into lithium and uranyl hydroxides. W. C. W.

Behaviour of Iodine and Arsenious Sulphide at High Temperatures. By R. SCHNEIDER (*J. pr. Chem.* [2], **23**, 486—488).—Preliminary notice. A mixture of (107 parts) realgar with (127 parts) iodine, heated out of contact with the air, melts very easily to a homogeneous brown-red fluid, without giving off iodine, and on cooling solidifies to a vitreous mass of the same colour. When powdered it looks like realgar, and is neither soluble in alcohol, carbon bisulphide, or chloroform, nor does it give up its iodine to these solvents; it melts slightly above 100° , and if air is excluded it distils without decomposition. This new compound is probably $AsI_3 \cdot As_2S_3$, similar to the antimony and bismuth iodosulphides, $SbI_3 \cdot Sb_2S_3$, and $BiI_3 \cdot Bi_2S_3$, described by the author (*Pogg. Ann.*, **110**, 147); they, however, crystallise well, whilst this could not be obtained crystalline. A mixture of $As_2S_3 + 4I$, when moderately warmed, melts to a homogeneous red-brown liquid, which slowly solidifies to an indistinct crystalline scarlet-red mass, moderately soluble in carbon bisulphide with a yellow-brown colour; from this solution the substance separates out as a vermilion-coloured crystalline crust. This compound appears to be $(AsI_3 \cdot As_2S_3)_2(SI_2)_3$, somewhat resembling the tin compound, $SnI_4 \cdot SnS_2 \cdot (SI_2)_2$, made by fusing tin sulphide with iodine, and described by the author (*ibid.*, **111**, 249). D. A. L.

Mineralogical Chemistry.

Formation of Moss-gold and Silver. By A. LIVERSIDGE (*Jahrb. f. Min.*, 1879, 622).—After roasting arsenopyrites in a muffle, the formation of moss-gold was observed, but it did not exactly resemble the naturally formed body. Moss-silver was obtained during the reduction of the chloride or sulphide in hydrogen at a temperature much below the melting point of silver. G. Bischof had, however, previously experimented in this direction. The author calls the phenomenon “crystallisation by thermo-reduction.” H. B.

Mode of Occurrence of Gold in Certain Minerals from the United States. By M. CHAPER (*Jahrb. f. Min.*, 1879, 605—606).—In the West African gold fields, where the gold occurs with different metallic sulphides in quartz veins, the usual amalgamating and washing processes are almost useless. The gold seems to occur partially at least as an ore. On treating the rock with nitric acid, a portion of the gold goes into solution and some native gold remains insoluble; also the rock freed from metallic sulphides by weathering is seen to contain small metallic gold particles. A pocket containing lead carbonate and iron oxides, the products of decomposition of galena and pyrites, was found to contain gold and silver in the same proportion as in the unaltered ores. The silver had been converted into chloride, but on removing this by a dilute solution of sodium thiosulphate, a considerable quantity of gold was also dissolved; the residue still contained here and there particles of metallic gold. H. B.

New Fossil Resins from East Prussia. By E. PIESZCZEK (*Arch. Pharm.* [3], 14, 433—436).—In the glauconitic sand of East Prussia certain resins are found together with amber; they occur in various shapes and sizes, and are known as “black” and “brown” resin. The black resin has a rough surface and is very brittle, breaking down to a cinnamon-coloured powder. The cleavage is conchoidal, lustre glassy, and of a deep black-brown colour. The brown resin occurs in drops, is tough, and contains at times plant remains, and the surface is of a light grey-brown. Solvents as benzene, alcohol, &c., have no effect on the black resin, but of the brown resin ether dissolves 1·2 per cent., and chloroform 1·0 per cent.; these solutions, on evaporation, leave a clear yellow aromatic varnish. Both resins are unattacked by alcoholic potash, and melt only when heated on platinum foil; at higher temperatures they burn with a smoky flame. Succinic acid is apparently absent from both, but a small quantity of sulphur is present. The ash of the “black” amounts to 1·65 per cent., that of the brown to 5·5; moisture is present to the amount of 3·4 and 4·5 per cent. Sp. gr. of the black is 1·175, of the brown, 1·126. Composition of black resin, C, 71·02; H, 8·15; O, 20·83. Composition of brown resin, C, 67·86; H, 8·56; O, 23·58. The name *Beckerite* is proposed for the brown resin, and *Stantienite* for the black. E. W. P.

Boghead Coal from Resiutta. By M. BUCHNER (*Dingl. polyt. J.*, 240, 76).—This coal, which occurs at Resiutta on the Ponteba Railway, has a brown colour, the powder being olive green; it is partly tough, partly slaty, and has a sp. gr. of 1·516. It burns with a large strongly luminous flame, and contains between 41·11 and 50·31 per cent. of ash. When it is subjected to ignition with exclusion of air, the residue is poor in carbon, and shows a heavy loss in weight (40·28 to 46·80 per cent. loss). The following is an analysis of this coal compared with English boghead and Wigan coal:—

	Calculated after deducting ash.	Resiutta.	English boghead according to Penny.	Wigan cannel.
Carbon.....	35·39	71·07	81·15	79·23
Hydrogen	3·83	7·20	11·24	6·08
Oxygen and nitrogen..	29·67	21·73	7·61	14·69
Ash	50·31	—	—	—

Boiling ether gives 1·75 per cent. of asphaltic residue, and benzene 1·45 per cent. The following are the volatile constituents obtained from this coal when subjected to destructive distillation, compared with English boghead coal and Bohemian anthracite:—

	Boghead from Resiutta.		Bohemian anthracite.	English bog- head coal.
	I.	II.		
Volatile constituents	40·88	46·80	50·14	68·51—69·10
Non-volatile carbon.	12·97	12·19	34·19	9·49—8·00
Ash.....	46·15	41·01	15·55	22·00—22·90

After deducting ash.

Volatile constituents	75·81	77·60	59·37	87·80—89·62
Non-volatile carbon.	24·19	22·40	40·63	12·20—10·38

D. B.

Some Bismuth Minerals from Nordmark, in Wermland. By H. SJÖGREN (*Jahrb. f. Min.*, 1879, 611—612).—(1.) *Native bismuth.*—It forms small druses or veins in white calcite, and is accompanied by pyrites and a green serpentine-like body; it contained:—

Bi.	Pb.	Fe.	S.
63·84	28·65	2·46	5·18 = 100·13

The percentage of sulphur is almost that required by the iron and lead to form FeS and PbS; hence the bismuth occurs as metal; this and the galena are easily seen side by side on preparing a polished surface. (2.) *Bjelkite.*—Steel-grey in colour, with a metallic lustre; texture fibrous; H. = 2·5—3; sp. gr. = 6·39—6·75; fuses easily. After deducting 2·19 per cent. gangue, it contained:—

Bi.	Pb.	Fe.	S.
42·40	40·30	1·01	16·29 = 100·00

corresponding to $2\text{PbS}.\text{Bi}_2\text{S}_3$. The author believes that the ferrous sulphide which Lundström considered as an essential constituent, to

have been only enclosed pyrites, and from the above analysis he concludes that this mineral is identical with cosalite and Frenzel's altered cosalite, viz., rezbanyite. (3.) *Galenobismuthite*.—This new mineral is compact or fibrous, tin-white, and has a strong metallic lustre; fracture uneven; streak greyish-black and shining; H. = 3–4; sp. gr. = 6·88; easily fused and reduced on charcoal. The mean of two analyses is:—

Bi.	Pb.	S.	Fe.
54·41	27·42	17·06	trace = 98·89

hence the formula $\text{PbS}, \text{Bi}_2\text{S}_3$. In both these minerals small particles of gold occur. H. B.

Occurrence of Cinnabar in California and Nevada. By W. P. BLAKE; and **The Occurrence of Mercury in California.** By G. ROLLAND (*Jahrb. f. Min.*, 1879, 604).—The occurrence of cinnabar in the siliceous deposits of warm springs, fumaroles, &c., has been repeatedly demonstrated, and according to the authors the great deposits of California and Nevada have originated similarly. The geysers in the latter locality are clearly situated along a fissure in the earth's surface. The Californian deposits occur equally in sedimentary and in eruptive rocks; the lodes reach a thickness of 150 meters and contain up to 35 per cent. The accompanying serpentine rocks are supposed to have been formed first, and to have prepared a passage for the mercurial vapours. The ore is often accompanied by opal containing 1–3 per cent. mercury. The cinnabar occurs in druses and in veins ramifying therefrom, compact and pure; crystals are seldom met with. The black sulphide metacinnabar, small quantities of metallic mercury in the upper layers, and some selenium compounds also occur there; and as accompanying minerals chalcedony, common opal, sulphur, metallic sulphides, the various products of hot springs and solfataras; also bituminous substances, amongst which Rolland describes two new species. H. B.

Analysis of Frieseite. By K. URBA (*Jahrb. f. Min.*, 1879, 620–621).—The author corrects an error in his former analysis of this mineral, and gives also a new analysis by K. Preis:—

	Ag.	Fe.	S.
I.	29·1	37·4	33·0 = 99·5
II.	27·6	37·3	33·9 = 98·8

Both these give the formula $\text{Ag}_2\text{Fe}_3\text{S}_8$. Streng has shown that all the known members of the “Sternbergit-silberkies” group, with the exception of frieseite, can be expressed by the formula $\text{Ag}_2\text{S} + p\text{Fe}_n\text{S}_{n+1}$, and accordingly can be considered as isomorphous mixtures of acanthite, Ag_2S , and pyrrhotite, $\text{Fe}_n\text{S}_{n+1}$. As the above exception is now removed, there only remains against Streng's hypothetical isomorphism of these last two minerals, the hexagonal nature of the latter. This point is by no means certain, as both Streng and the author have shown that pyrrhotite is probably rhombic. H. B.

Note on Chrome-iron. By J. THOULET (*Jahrb. f. Min.*, 1879, 616—617).—Fisher has shown that this body is not opaque, but in the thinnest sections transparent, with a brownish-red or red colour. The author has come independently to the same conclusion. A polished surface polarised reflected light like a transparent body. The angle of most perfect polarisation was $64^{\circ} 30'$, hence $\mu = 2.065$. It is possible that the anomalies observed when light is reflected by some apparently opaque bodies may be similarly explained.

H. B.

Production of a Crystallised Iron Phosphide and of Anorthite by the Fires in the Coal Beds at Commentry. By E. MALLARD (*Compt. rend.*, 92, 933—935).—In a fire which occurred in the coal mines at Commentry the schists which formed the roof of the coal beds became fused, and disseminated through this fused mass a brittle steel-grey magnetic substance was found, almost as hard as steel; sp. gr. = 6.72. It has the composition Fe, 84.28; P, 12.10; As, 1.65; S, 1.75; C, traces = 99.78, which, neglecting the arsenic, and regarding the sulphur as existing in the form of ferrous sulphide, agrees closely with the formula Fe_7P_2 . With dilute acids it at once gives off hydrogen sulphide, the phosphide being decomposed afterwards with greater difficulty. The iron phosphide occurs disseminated through the fused rock in small rounded grains, and is also found in more or less crystalline masses as large as a man's fist. Some specimens are distinctly crystallised, having the form of a square prism, modified by the slightly developed faces of the tangent prism, and terminated by a somewhat truncated pyramid. This substance is probably identical with the iron phosphide prepared by Sidot, and with the phosphide found in the Branau meteorite by G. Rose, who gave to it the name *rhabdite*, a name which may be conveniently retained. The rock which forms the gangue of the phosphide has a greyish-brown colour, is compact, with a granular and sub-crystalline fracture, and contains cavities, some of which are lined with some crystalline substance. It contains fragments of coke, some of which are very pure, have a brilliant conchoidal fracture, and scratch glass, but not quartz. Optical and chemical examination shows that the rock consist largely of interlaced and twinned needles of anorthite, which also occurs in very thin, distinctly crystalline, opalescent plates, lining the cavities, and sometimes found in the mass of the rock. In addition to iron phosphide, anorthite, and amorphous fused matter, the altered rock contains irregular grains of pyroxene. In structure and general character, it resembles certain volcanic rocks and meteorites. The rock forming the gangue of the beautiful specimens of *vivianite* found at Commentry some time ago has exactly the same structure and character as the rock forming the gangue of *rhabdite*, and it is probable therefore that the *vivianite* is a product of the alteration of the latter. The iron in the phosphide has been derived from the nodules of ferrous carbonate occurring in the coal and in the schists: the phosphorus has probably been derived from the same source.

C. H. B.

Manganese-calcium Carbonate containing Barium from Laangban. By H. SJÖGREN (*Jahrb. f. Min.*, 1879, 612).—Reddish

grains, with distinct rhombohedral cleavage, imbedded in crystalline granular limestone. On analysis, the following numbers were obtained :—

BaCO ₃ .	MnCO ₃ .	CaCO ₃ .
2·04	10·06	87·14 = 99·24

H. B.

Aluminite from Mühlhausen, near Krulup, in Bohemia. By R. RAFFELT (*Jahrb. f. Min.*, 1879, 615).—The masses of this mineral have exactly their theoretical composition, viz., Al₂O₃.SO₃ + 9H₂O.

H. B.

Chalcomenite, a New Mineral. By DES CLOIZEAUX and DAMOUR (*Compt. rend.* 92, 837—840).—Chalcomenite, a copper selenite, occurs in the form of thin crusts, composed of very small transparent blue crystals. It is found lining the cracks in the deposits of lead selenide at Cachenta, Argentine Republic, and can be easily distinguished from the coating of malachite and azurite with which the selenide is often covered. It is insoluble in water, but dissolves in dilute acids. When heated it blackens, and gives off a little water. The crystals are monoclinic, the general form being a very slightly oblique prism of 108°, modified by simple combinations. The plane of the optical axes is parallel, and the crystals have a strong dispersive power. Measurements of the angles of different faces are given. Chalcomenite is in all probability identical with the crystalline copper selenite obtained by Friedel and Sarasin.

C. H. B.

Note on Cabrerite from Laurium. By DES CLOIZEAUX and A. DAMOUR (*Jahrb. f. Min.*, 1879, 593—594).—In the zinc mines of Laurium cabrerite has been found, as well as adamine, and in a manner exactly corresponding with its occurrence in the Sierra Cabrerita. Cleavage $\infty P\infty$, as in cobalt bloom. The faces 0P and $\infty P\infty$ inclose an angle of 125°—125° 20'; in cobalt bloom it is 124° 51'. These two are also optically isomorphous; the planes of the optical axes are at right angles to $\infty P\infty$, and make the following angles with—

	Axis ϵ' .	Axis \bar{a} .
Cabrerite from { Laurium	35° 55'	19° 5'
{ Spain	34 20	20 20
Cobalt bloom (new measurements)	34 12	20 57

white light being used. Dispersion of the axes $\rho > v$, strongly marked, as is also the crossed dispersion. Measured in red light the apparent angle is 105° 30'—106° 32', and on the Spanish specimens 110° 20'—112° 30'. Colour, beautiful apple-green; on the cleavage face pearly lustre. H. = 1; sp. gr. = 3·11, and those from Spain 2·96. On analysis the following numbers were obtained :—

As ₂ O ₅ .	NiO.	CoO.	MgO.	FeO.	H ₂ O.
41·40	28·72	trace	4·64	2·01	23·11 = 99·88

giving the formula R₃As₂O₈ + 8Aq. This, coupled with the crystallographical and optical determinations, shows that cabrerite is a variety of nickel arseniate, or annabergite.

H. B.

Felspars from the Valley of Bagnères-de-Luchon (Upper Garonne). By E. FILHOL (*Compt. rend.*, 92, 1059—1060).—In a treatise on the mineral waters of the Pyrenees, published in 1853, the author states that while the granitic rocks from which the hot springs emerge are generally considered to contain potash felspar, the waters themselves contain principally sodium salts. He has recently made analyses of the rocks in the neighbourhood, and finds, with the aid of a polariscope, that the felspar is principally microclitic, with small veins of albite running through it. J. I. W.

Note on Mica, more especially Zinnwaldite. By H. BAUMHAUER (*Jahrb. f. Min.*, 1879, 600—601).—Plates of zinnwaldite show streaks and yellowish coloured zones, which are parallel to the combination edges of the basal plane with the border faces, viz., $\infty P\infty$, $2P\infty$, and $+P$. Parallel to these zones are numerous fine internal streaks, which are more evident in plane polarised light, but behave differently among themselves. Those parallel to the edge $+P:0P$ are seen best with crossed Nicols and the plate in a depolarising position; those parallel to the edges $0P:\infty P\infty$ and $0P:2P\infty$ cannot be thus seen, but appear when viewed between parallel Nicols and with the band inclined 45° to the plane of polarisation. These zonal bands the author considers are due, not to interposition of foreign material, but to some peculiar and irregular arrangement of the zinnwaldite molecules. Plates of this mineral subjected to etching with hydrofluoric acid or fused alkali, yield sharply defined five- or six-sided etching figures lying on opposite faces of the plates, not as they would on an asymmetrical, but as on a monosymmetrical crystal. In these figures two pairs of sides are parallel to two arms of the fracture figure (*Schlagfigur*); the smallest pair of faces—or single face—lies inclined to all these arms, and moreover the pair of middle length is always parallel to the edge $0P:\infty P\infty$. These etching figures vary in position on different parts of the plate, but so that they lie symmetrically to a line parallel to $0P:\infty P\infty$, and the two halves are divided by a jagged line running in this direction. From such behaviour, the author still considers zinnwaldite as monosymmetrical and not asymmetrical. Muscovite similarly treated yields similar etching figures.

H. B.

Microscopic Study of the Glasses resulting from the Fusion of the Ashes of Grass, &c. By C. VÉLAIN (*Jahrb. f. Min.*, 1879, 623—625).—A glass resulting from the burning of a corn stack was examined. It is apparently structureless, deep coloured, full of bubbles, and contains water. To remove unburnt particles, it was fused for a long time, and then found to contain—

SiO ₂ .	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.
62.9	3.1	5.7	1.9	15.8	3.9	4.3	2.2 = 99.8

The alumina probably came from the clay bottom of the stack. In section the glass consists of light and darker streaks, owing to the separation of minute crystals. In the light streaks are globules, apparently opal, but on the surface and near the bubbles the silica occurs as tridyl-

mite. The separated crystals, often not very well defined, are—green augite, tabular through $\infty P\infty$; a yellowish-green body, probably one of the monosymmetrical pyroxenes; colourless crystals, probably diopside; anorthite in twin crystals, around which the later formed pyroxene crystals are grouped; wollastonite and apatite. Round the cavities are hyalite and opal, or else a film of opal accompanied by tridymite. In a dark coloured glass from a burnt oat stack, the augites were tabular through OP, and felspar and apatite were absent. In a spongy glass from a hayrick there were but few crystals, and these consisted of augite and wollastonite.

H. B.

Serpentine from Verrayes, in the Valley of Aosta. By A. COSSA (*Jahrb. f. Min.*, 1879, 662—663).—The exact locality where this noble serpentine occurs is not known. It is green, with aggregations of magnetic iron particles, which are seldom crystalline. The aggregations, which distinguish this serpentine from others found in Piedmont, inclose a crystalline substance of a milk-white colour. Under the microscope these crystals prove to be rhombic. They were isolated by removing from the powdered mineral, first the magnetite by a magnet, and then the serpentine by hydrochloric acid. The remaining crystalline powder contained magnesia, silica, and traces of lime and chromium; it is probably enstatite. Analyses of this serpentine and those from Corio and Favaro are given. No traces of olivine were found, but still the author considers olivine as having been the original mineral. By fusion a mass was obtained, consisting on the surface of olivine crystals, and in the interior of enstatite crystals. By fusing together silica and magnesia, the author obtained dendritic crystals having the composition of enstatite, $MgSiO_3$.

H. B.

Note on Titaniferous Peridot from Zermatt. By A. DAMOUR (*Jahrb. f. Min.*, 1879, 594—595).—This variety of olivine was originally found by the author at Pfunders, in the Tyrol; he has also found it on the Findelen glacier, near Zermatt. On analysis they gave—

	SiO ₂ .	TiO ₂ .	MgO.	FeO.	MnO.	H ₂ O and volatile.
Zermatt ..	36.14	6.10	48.31	6.89	0.19	2.23 = 99.86
Pfunders ..	36.30	5.30	49.65	6.00	0.60	1.75 = 99.60

That from Zermatt occurs in nests and particles in veins of calcspar in talcschiefer. In colour it is pure garnet-red, and has an orange-yellow streak. In thin splinters it is transparent, and shows pleochroismus. H. = 6.5; sp. gr. = 3.27. It shows no distinct crystalline form.

H. B.

Halloysite from Tüffer. By K. JOHN (*Jahrb. f. Min.*, 1879, 614—615).—It occurs in irregular masses; in the centre it is half-transparent like talc, around this is a pure white fatty-feeling mass, and on the surface an earthy crumbling mass. On analysis these three portions yielded the following numbers:—

	SiO ₂ .	Al ₂ O ₃ .	H ₂ O at 100°.	H ₂ O above 100°.
I.	38·37	33·31	15·75	13·05 = 100·48
II.	38·68	33·02	14·97	13·23 = 99·90
III.	40·07	34·53	13·23	13·50 = 100·40

Thus the innermost portion contains the most water, but after long standing in the air it contains only 21·5 per cent. ; all, however, attain a constant state of hydration at 100°, and have then the composition of kaolin, but they have not its properties, hence the author considers it as halloysite, although its composition does not exactly correspond.

H. B.

Russian Topaz and Enstatite from Snarum. By G. SELIGMANN (*Jahrb. f. Min.*, 1879, 606—607).—The topaz crystals—probably from the Ilmengebirge—show no point of attachment. They exhibit numerous faces, and are of two types (1), tabular through the abnormal growth of two faces of $\infty P\bar{2}$; (2) pyramidal, the prismatic faces being almost absent. In both cases, the prismatic faces alone are smooth; on the brachydomes are numerous subindividuals, and on the basal plane are six-sided depressions caused by a pyramid and a brachydome.

The enstatite crystals, now converted into steatite, are undoubtedly rhombic with the forms $\infty P\infty$, $\infty P\infty$, ∞P , $\frac{1}{2}P\infty$ and $P\bar{2}$, and also the angles are those of enstatite. These crystals were described by Helland as being pseudomorphs after augite.

H. B.

Spodumene and Petalite. By C. DOELTER (*Jahrb. f. Min.*, 1879, 602—604).—Spodumene is crystallographically analogous to the augite group, but its composition $3Li_2SiO_3 + 4Al_2Si_3O_9$ (Rammelsberg) is not analogous to that of akmite and aegrine, viz. :—



to which it is nearly related. The author therefore has analysed fresh and suitable specimens from Norwich (N. America) and from Brazil, decomposing by pure hydrofluoric acid, and taking special precautions against the lithia being carried down with the alumina, &c.; in both cases the results led almost exactly to the formula—



the sample from Brazil contained a small quantity of soda. The author considers that in all published analyses of petalite, the lithia determinations are too low; in geometrical and physical properties, it corresponds with spodumene, and seems to bear chemically the same relation to this mineral as anorthite does to albite, *i.e.*, the group $Li_2Al''_2$ is isomorphously replaced by Si^{iv}_2 .* The author, however, had no fit material for a new examination.

H. B.

Artificial Pyroxene (Diopside). By L. GRUNER (*Jahrb. f. Min.*, 1879, 623).—In order to harden some bricks made from a limestone containing alumina and magnesia, they were heated several days in a blast oven. The oven walls were rich in silica, those bricks touching the oven bottom were fused and a network of shining grey needles of diopside had formed. Their forms were ∞P , $\infty P\infty$, $2P$ and P ; the

* Compare Abstr., Phillipsite, p. 695.

angles were those of diopside. Analyses of these crystals and of the bricks are given. H. B.

Stilbite (Heulandite) from Kerguelen's Island. By A. LIVERSIDGE (*Proc. Roy. Soc. Edin.*, 11, 117—119).—The specimens which occur in the seams of amygdaloid, are semitransparent and colourless, the crystals ($\frac{1}{2}$ inch long), which grow as an incrustation $\frac{1}{8}$ — $\frac{3}{10}$ inch thick, are brittle and cleave parallel to the brachy-diagonal, less readily parallel to the macro-diagonal.

The best developed faces are the brachy- and macro-pinacoids, capped with pyramidal planes; the brachy-pinacoid is the most developed, and the basal pinacoids least. Hardness 4. Sp. gr. 2.24—2.25; in powder 2.29. Soluble without gelatinising in hydrochloric acid. The lower crust does not appear to be quite the same, most probably sphærostilbite. Formula, $\text{Al}_2\text{O}_3.3\text{SiO}_2 + \left. \begin{array}{l} \frac{5}{6}\text{CaO} \\ \frac{1}{6}\text{Na}_2\text{O} \end{array} \right\} 3\text{SiO}_2 + 6\text{H}_2\text{O}.$ E. W. P.

The So-called Hypersthene-Andesite from St. Egidii in Lower Styria. By E. HUSSAK (*Jahrb. f. Min.*, 1879, 661—662).—The author confirms the greater part of Niedzwiedzki's observations on this tertiary eruptive rock, but finds that the constituent formerly considered as hypersthene (because of cleavage, pleochroism, and position of the optical axes) is not rhombic, and hence is probably augite. The cleavage-faces he considers as prismatic and not pinacoidal, *i.e.*, they enclose an angle of $87^\circ 6'$ instead of 90° , a rather fine point to determine under the circumstances. Finally, the author makes the remarkable statement that “in sections parallel to the clinopinacoid the vibration-directions are not perpendicular to one another, so that the mineral possesses not rectangular but inclined depolarisation directions, which is the case with a monosymmetrical but not with a rhombic augite,” and consequently considerable doubt rests upon the conclusion that “the name hypersthene-andesite should be rejected.” H. B.

Phillipsite and its Relations to Harmotome and Desmin. By W. FRESSENIUS (*Jahrb. f. Min.*, 1879, 596—599).—The author has repeated Baumhauer's experiments on harmotome, verifying the optical irregularities, but since the plane of the optic axes makes 60° with Naumann's brachypinacoid, he considers that no doubt can rest upon its monosymmetric character. The peculiar growth and irregularities of harmotome crystals render it impossible to determine by their geometrical form if they belong to the monosymmetric system. But this the author has determined by optical examination of clear crystals from Nidda, with deeply furrowed edges. Placing the monosymmetric phillipsite in the position proposed by Streng, so as to show its relation to harmotome, the axial relations are in mean $a : b : c = 0.714 : 1 : 1.2113$ and $\beta = 55^\circ 40'$, whereby $\infty P\infty$, $\infty P\infty$ and P of the rhombically placed crystals become $0P$, $\infty R\infty$, and ∞P in the new position. In a section parallel to $\infty R\infty$, the directions of vibration could not be determined exactly, owing to internal tensions; in such a section, the angle between the planes of the optical axes of the two

interpenetrating crystals varies from $20^{\circ} 58'$ to $24^{\circ} 34'$, mean $22^{\circ} 31'$ for sodium light; for lithium light the angle is about 1° smaller. From one arm of a crystal, a plate perpendicular to OP and $\infty R\infty$ was cut, and showed the acute optic axial angle to be 94° in oil, and the obtuse angle seen through $\infty R\infty$ was 130° , thus making the true optical axial angle about 64° ; the plane of the optic axes is inclined about 10° to the clino-axis in the angle β .

By analysis of very carefully selected material from different localities, the author finds the variation of composition to be a fact, and consequently all varieties cannot be classed under one general formula. Crystals from the Kaiserstuhl were analysed by the author for the first time; after drying at 100° they contained:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	BaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.
53.94	18.97	0.26	5.60	0.41	0.31	4.88	0.98	14.62 = 99.97

The samples from Annerode and the Kaiserstuhl are analogous in composition to phillipsite, and are accordingly truly isomorphous. According to the author the amount of water varies with the temperature and moistness of the air, and the heated but not ignited powder reabsorbs all its lost moisture from the air; if this be true, the amount of water in this and other zeolites will not have any simple relation to the other constituents.

Taking the recent view of von Lasaulx that desmin and phillipsite are isomorphous, the author explains the variations in composition on the ground of isomorphous mixtures. Streng has written the formulæ of albite and anorthite, in order to show the similarity in composition; thus:—

Albite	R''	Al ₂	Si ₂	Si ₄	O ₁₆
Anorthite. . . .	R''	Al ₂	R''Al ₂	Si ₄	O ₁₆

where R'' denotes any mixture of Ca and Na₂, and the octovalent Si₂ is isomorphous with octavalent R''Al₂. Albite and anorthite are isomorphous, and the composition of any mixture is expressed thus—

$$x(R''Al_2Si_2Si_4O_{16}) + y(R''Al_2R''Al_2Si_4O_{16})$$

and these silicates when hydrated form, according to the author, either (1) chabasite or (2) phillipsite and desmin, *i.e.*,

1. $x(R''Al_2Si_2Si_4O_{16} + 8H_2O) + y(R''Al_2R''Al_2Si_4O_{16} + 8H_2O)$.
2. $x(R''Al_2Si_2Si_4O_{16} + 6H_2O) + y(R''Al_2R''Al_2Si_4O_{16} + 6H_2O)$.

It is to be remarked that when chabasite and phillipsite occur together, they are both rich or both poor in silica, thus tending to show that they are different hydrates deposited from one solution, and owe their origin to slight variations in circumstances.

H. B.

Note on Zinc-Spinelle from Brazil. By A. DAMOUR (*Jahrb. f. Min.*, 1879, 594.)—From the diamond sand of Minas-Geraes the author obtained small pieces and crystals of this substance, having the form $O.\infty O$, the faces of the latter being striated parallel to their longer diagonal. Colour yellow, bluish-green and blue, appearing in candle-

light deep red, pale green and blue. Their sp. grs. are 4·56, 4·54 and 4·52. H. = 8. Before the blowpipe infusible, and colourless while hot. Those appearing red by lamp-light contained—

Al ₂ O ₃ .	ZnO.	FeO.	Volatile.
59·41	33·82	6·41	0·14 = 99·54

H. B.

Analysis of Demantoid from the Urals. By J. WALLER (*Jahrb. f. Min.*, 1879, 610—611).—The author describes the origin of the name demantoid and the occurrence of this beautiful green stone in the platinum washings of Jekaterinburg. The mean of three analyses on samples from Bobrowka is:—

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	CuO.	MgO.	K ₂ O.	Na ₂ O.
35·69	29·96	0·19	1·25	32·33	0·08	0·25	0·63 = 100·38

Manganese, chromium, and water were absent. The oxygen ratio of RO : R₂O₃ : SiO₂ is 1·07 : 1 : 2·10, and it is accordingly a characteristic iron-lime garnet.

H. B.

Artificial Production of Ophitic Structure. By F. FOUQUÉ and A. M. LÉVY (*Compt. rend.*, 92, 890—891).—The ophitic rocks of the Pyrenees are characterised by the development of microliths of triclinic feldspar embedded in elongated layers of pyroxene. The microliths of augite found in trachytoidal rocks seem to have had time, in the ophites, to agglomerate after the solidification of the feldspar, forming large crystals which resemble in appearance the augite crystals of the first stage of solidification of trachytoidal rocks. The authors have produced this peculiar structure artificially by heating a mixture of anorthite and augite to white-redness, annealing, and then annealing again at bright redness. The first annealing causes the solidification of the anorthite, the second that of the augite. When labradorite was used in place of anorthite, the labradoritic ophite obtained showed the passage from trachytoidal to ophitic structure, a result which agrees with Bréon's observation that in Iceland beds of ophitic dolerites alternate with beds of labradorite, and that the one rock frequently passes into the other. Eucritic meteorites and the dolerite containing the native iron at Ovifak, have an analogous structure and mineralogical composition.

C. H. B.

Mineralogical Notes, No. V. The Occurrence of Manganese in Nordmark. By A. SJÖGREN (*Jahrb. f. Min.*, 1879, 612—614). The author gives a detailed account of the veins in the Mossgrube, Nordmark. The deposits, which occur in limestone rocks, are sometimes 70 cm. thick; above are chloritic rocks, below are limestones. With assistance of the microscope the following minerals have been detected:—(1.) *Manganosite*: Microscopic crystals in limestone, dolomite, or brucite, with predominating hausmannite. In a limestone coloured brown through manganese, it occurs in a perfectly fresh condition, but when accompanied by pyrochroite it is more or less oxidised. The forms $O \cdot \infty O$, and sometimes $\infty O \infty \cdot O$ were observed. (2.) *Pyrochroite*: Crystallised in six-sided prisms 3—4 mm. long, and

1—1½ mm. broad; colourless; glassy lustre, but on the basal plane a pearly lustre. Oxidises easily, especially on heating. They contain 75·3 per cent. MnO and 20·6 per cent. H₂O. It more often occurs in foliated masses, oxidising exceedingly readily. Generally occurs with brucite and olivine, but never with fresh manganosite, and the author therefore considers it to have been formed after the vein itself. (3.) *Brucite*. (4.) *Hausmannite* as principal ore. (5.) *Olivin*, in microscopic particles, showing beginning of decomposition. It occurs with pyrochroite, never with manganosite, and hence is a secondary product. (6.) *Manganese carbonate*, as secondary product. (7.) *Barytes*. (8.) *Hornblende*, in small microscopic crystals. (9.) *Lime-iron garnets*, also a secondary product, in greenish-yellow crystals, form ∞O. In conclusion, the manganosite, brucite, and calcite were first deposited, then oxidation and hydration occurred, yielding pyrochroite and manganese carbonate, a portion of the brucite remaining unchanged, and the last product formed was the olivine. These deposits have a great analogy to those of Laangban, but in the one case oxidation has occurred only in certain clefts, in the other throughout the whole vein. To this paper Nordenskiöld adds that pyrochroite occurs in masses of a hundred pounds weight, and gives a couple of analyses. H. B.

Mineral Analyses. By T. HIORTDAHL (*Jahrb. f. Min.*, 1879, 607—609).—These analyses of Swedish rocks and minerals were made upon:—(1.) The anorthite and olivine constituting an olivin-gabbro; the brownish-yellow olivin grains are very rich in iron containing 24·02 per cent. FeO. (2.) Five specimens of saussurite-gabbro. (3.) Nodules of supposed anthrophyllite, which the author on the ground of his analysis regards as hypersthene, but without giving any physical data, which alone are capable of deciding the point. (4.) A silurian limestone containing, besides iron and magnesium carbonates, alumina, &c.; also 0·10 per cent. C, 6·67 per cent. ZnS, and 0·83 per cent. FeS. H. B.

The Mountain Group of the Rummelsberg, near Strehlen. By E. SCHUMACHER (*Jahrb. f. Min.*, 1879, 642—644).—The author describes the following rocks from this district more minutely than has been done in the geological survey, viz., granite, microgranite, gneiss, hornblendeschiefer, quartzite, glimmerschiefer, talkschiefer, and granular limestone. H. B.

Occurrence of Propylite in Transylvania. By C. DOELTER (*Jahrb. f. Min.*, 1879, 648—652).—Richthofen (1868) gave the name propylite to a rock characterised by its dioritic appearance, differing from the newer eruptive rocks by its porphyry-like structure and by its green colour; it is one of the oldest eruptive rocks of the tertiary period, and does not appear as a lava. It consists essentially of a dense asymmetrical felspar, oligoclase, hornblende, generally green and fibrous, titaniferous magnetite, and of augite and quartz, which sometimes become essential constituents; and thus there are the following varieties: quartz-propylite, hornblende-propylite, and augite-propylite. According to Richthofen, the quartz-propylite is

the same as Hauer and Stache's dacite (1863) from Transylvania, but these authors use dacite as a collective name for andesite-quartz-trachyte, for granite-porphyrific quartz-trachyte, and for quartz-trachytes resembling greenstone, and of these only the last variety corresponds to quartz-propylite. Thus Richthofen, in identifying propylite with dacite, gave the first a broader meaning, which was not his intention. Zirkel afterwards (1876) endeavoured to place propylite in the list of recognised rocks, and found a difficulty in sharply defining it; he recognised in all essential chemical and physical details the identity of propylite and amphibole-andesite, and of quartz-propylite and quartziferous amphibole-andesite (which Zirkel calls dacite), but still believed them to have separating differences. Thus dacite with each of these authors bears a different meaning. These separating differences of Zirkel, H. Rosenbusch shows however to vary, and to be only constant in the occurrences of one and the same district, or to be of a purely secondary and consequently unimportant nature; on mineralogical grounds he therefore no longer holds separated propylite and amphibole-andesite, either in their quartz free or quartz containing varieties. From a geological point of view it will be impossible to discuss the small differences in the ages of these rocks, until we have more accurate means of doing so than at present. Doelter shows that the propylite and quartz-propylite from Transylvania resemble no other occurrence exactly, but stand between Zirkel's propylite and his amphibole-andesite; and that the ores in this locality are not always confined to characteristic propylite. Further researches are required to prove that this propylite is no typical rock, but a variety of amphibole-andesite or of augite-andesite, either with or without admixture of quartz. H. B.

Piperno. By E. KALKOWSKÝ (*Jahrb. f. Min.*, 1879, 645—648).—This rock, from the workings near Pianura and near Soccavo by Naples, has been classed as phonolite and as a trachyte; the author confirms the latter view. The constituent minerals are augite, magnetite, apatite, monosymmetric and asymmetric feldspars, sodalite, marialite, and glassy globules, and in clefts are sometimes hornblende, and sometimes nephelin needles. The rock is remarkable on account of numerous dark-coloured, elliptical and pointed patches, which are arranged in horizontal layers parallel to the under and upper contact faces with the other lava streams. The augite occurs in very small crystals, but sometimes in much larger ones grouped together, the whole group exhibiting a superficial zonal structure. The apatite occurs exceedingly sparingly. Large plagioclase and sanidin crystals predominate, and the latter also occurs throughout the ground mass in small crystals rich in enclosures. The glassy particles are free from enclosures, and seem to form an original constituent of the rock. The sodalite is not an essential constituent, for it exists in minute cavities between the feldspar crystals, and is a secondary formation. The marialite occurs only sparingly, contains numerous enclosures, and, according to the author, is identical with mizzonite. The magnetic iron occurs in small crystals singly and collectively. The dark flame-like patches contain more magnetite, and are more porous than

the general mass. Further, they contain radial and spherical aggregations of sanidin crystals, not previously observed in trachytes; there is no sudden change from these dark patches to the mass of the rock, and therefore they are not foreign enclosures, but there are enclosures of pieces of piperno which have suffered alteration at the time of the eruption. From his observations, the author draws the history of the formation of this remarkable rock: From the original homogeneous magma there separated first a part of the magnetite, partially scattered and partially collected together, and the larger augite and sanidin crystals; then while cooling an eruption took place, and this lava was thrown out. This caused the aggregations of magnetite to be drawn out and broken, and the sanidin crystals already formed to grow further, but to enclose magnetite and augite; the residuary magma becoming richer in silica, the glassy particles separated, and in those portions containing the collections of magnetite crystals, numerous sanidin needles separated and grouped themselves radially. Finally, the sodalite was formed by the action of fumaroles, and the external alteration of the augite crystals took place; the nephelin and amphibole were subsequently formed in clefts and pores. H. B.

Changes produced by Weathering of Phonolite. By C. v. ECKENBRECHER (*Bied. Centr.*, 1881, 61).—The first change experienced by phonolite is increase of silica, but this decreases as weathering proceeds. In the first stages the nephelin is zeolitised, as well as sodalite; in the second and third stages, kaolinisation of the felspars, and removal of the zeolites occur. E. W. P.

Presence of Phosphorus in the Rocks of Brittany. By G. LECHARTIER (*Compt. rend.*, 91, 820—822).—Seeing that phosphatic manures are now very generally used in Brittany, and that it does not seem possible to raise satisfactory crops without them, the author concluded that the soil of Brittany must be unusually deficient in phosphorus. An investigation of the rocks from which the soil is mainly derived, consisting chiefly of granites and schists, has shown that the proportion of phosphoric acid varies from 1 to 2 grams per kilo. in the granites of Ile-et-Vilaine, Côtes du Nord, Morbihan, Finistère, and Manche; with respect to the schists, although phosphoric acid is never wholly absent, it is much more variable than in the granite rocks, and is sometimes very small in quantity. The grey and blue tinted schists contain about 1 or 2 parts per thousand, whilst the compact violet-red specimens, which are used as building stone, contain scarcely one-half part of phosphoric acid per thousand parts of schist.

It is probable, therefore, that the soil proper of Brittany varies in its richness of phosphoric acid, according as it results from the disintegration of one or other of these rocks, and an analysis of the unmanured arable land is at present only wanting, in order to confirm the conclusions drawn from the examination of the rock specimens.

J. W.

Products of the Volcano, Monte Ferru (Sardinia). By C. DOELTER (*Jahrb. f. Min.*, 1879, 652—656).—This is a continuation of

a previous paper (*Jahrb. f. Min.*, 1878, 668), and in it many of the former assertions are recalled or modified; it consists of a very long series of rock sections, with some analyses. The rocks arranged in the order of their times of eruption are obsidian, sanidin-trachyte, amphibole, andesite, sanidin-plagioclase-trachyte, augite-trachyte, phonolyte, plagioclase-basalt with and without olivine and leucite-basalt; and here, as in other localities, the age and the acidity approximately correspond.
H. B.

A Group of Dissimilar Eruptive Rocks in Campton, New Hampshire. By G. W. HAWES (*Jahrb. f. Min.*, 1879, 644—645).—Near Plymouth the Pemigewasset flows through a gulley in a hill consisting of mica-slate. The walls of this gulley cut perpendicularly through five dykes of eruptive rocks, which, though similar in geological position, have very different compositions. The first is a normal diabase with numerous cavities (mandelstein) containing calcite and analcime, but the stone is no longer fresh; the second is a compact diorite; the third and fourth are of a whitish rock, consisting of orthoclase crystals, and with the spaces between filled up with iron oxides and calcite, rarely quartz; these seem to have been formed by the decomposition of hornblende; the fifth is a dense olivin-diabase, with a porphyritic appearance imparted to it by the augite and olivine, it contains also brown hornblende, only a few cavities are present, and these are filled with calcite, sphaerosiderite, and analcime. Analyses of these rocks are given; all but Nos. 3 and 4 contain from 2—4 per cent. titanic acid.
H. B.

Some Lavas from the Island of Niuafoou, and Communications on the Island of Futuna. By A. WICHMANN (*Jahrb. f. Min.*, 1879, 663—664).—At an eruption in April, 1867, on the island of Niuafoou (Tonga-Archipelago), the lava consisted of a very glassy augite-andesite, and the ashes of sharp-cornered glassy particles and discs, or of hair-like needles, with or without products of fusion. On the island Futuna, hyalomelane occurs in a small vein in a coral limestone, and also as a breccia. The hyalomelane contains plagioclase, olivine, and sometimes augite. The cement is a clayey substance, free from lime. A red clay, free from lime and organic remains, is sometimes eaten by the inhabitants.
H. B.

Lavas from the Neighbourhood of Catania. By L. RICCIARDI (*Gazzetta*, 11, 138—165).—The lavas from Etna consist principally of labradorite and augite; in limited quantity, magnetite, olivine, and apatite, more rarely hornblende, and mica very seldom. They all have an alkaline reaction, fuse readily, and are attracted by the magnet; the iron is present for the most part in the ferrous state. In the paper full details are given of the methods of analysis employed, all of which, however, are those ordinarily in use. The following is a description of the lavas analysed by the author, and a table of the analyses:—

Analyses.

	I.	II.	III.	IV.	V.	VI.
SiO ₂	46·05	50·23	50·30	51·73	55·66	49·63
TiO ₂	0·47	0·31	0·38	0·54	0·33	0·47
SO ₃	0·23	0·08	0·11	0·21	0·06	0·17
P ₂ O ₅	2·65	3·16	3·21	3·65	3·67	3·07
Cl	trace	trace	trace	trace	trace	0·00
FeO	11·18	10·48	12·05	11·23	10·83	10·93
MnO	0·59	0·52	0·49	0·71	0·43	0·36
Al ₂ O ₃	19·29	15·55	14·67	14·68	11·03	15·27
CaO	10·81	11·73	10·72	9·78	11·13	10·87
MgO	3·69	5·09	5·35	4·11	4·76	4·65
K ₂ O	0·73	0·51	0·56	1·24	0·48	1·49
Na ₂ O	3·55	2·78	2·63	2·98	2·37	2·82
Loss on ignition ..	1·03	0·45	0·21	0·48	0·26	0·35

	VII.	VIII.	IX.	X.	XI.	XII.
SiO ₂	49·43	52·09	50·61	49·27	49·17	49·66
TiO ₂	0·62	0·37	0·51	1·02	0·49	0·67
SO ₃	0·29	0·16	0·15	trace	0·09	0·11
P ₂ O ₅	3·00	3·22	1·80	3·47	3·21	1·71
Cl	trace	trace		trace	trace	trace
FeO	12·09	11·61	10·67	11·08	10·64	12·07
MnO	0·39	0·32	0·52	0·41	0·58	0·63
Al ₂ O ₃	16·83	16·58	15·67	15·06	20·53	18·08
CaO	9·57	9·13	11·35	11·28	9·81	9·60
MgO	3·91	3·13	5·10	4·51	2·21	4·21
K ₂ O	0·88	0·89	0·67	0·51	0·88	0·84
Na ₂ O	2·43	2·47	3·42	1·59	2·89	2·49
Loss on ignition ..	0·69	0·64	0·10	0·76	0·22	0·37

I. Lava Larmisi is a dark grey porous mass, sp. gr. 2·781, in which are disseminated small crystals of olivine, and acicular crystals of labradorite.

II. Lava dell' Ognina is porous and of a grey colour; sp. gr. 2·811.

III. Ancient lava, underlying that of the Rotolo, probably belonging to the lava dell' Ognina: this is of a pale grey colour, homogeneous and compact; sp. gr. 2·813.

IV. Lava Fratellipii, compact, of a grey colour; sp. gr. 2·681.

V. Lava del ponte dell' Ognina is very compact and homogeneous, in which a few acicular crystals of labradorite can be discerned, and very rarely pyroxene; sp. gr. 2·658.

VI. Lava Carvana (122 B.C.). This is tolerably compact, but the different mineral constituents can be clearly discerned, labradorite predominating. It is of a pale grey colour; sp. gr. 2·835.

VII. Lava di Cifali (A.D. 253). Pale grey, with very fine augite crystals disseminated in groups; sp. gr. 2·769.

VIII. Lava del Rotolo (A.D. 1381). This lava is pale grey, and somewhat compact, with druses of olivine, pyroxene, and felspar crystals—the latter predominating; sp. gr. 2·793.

IX. Lava del Crocifisso (A.D. 1381). Dark grey, with white crystals of labradorite; sp. gr. 2·664.

X. Lava of the great eruption of 1669. This lava stream is 14 miles long and 3 to 4 broad, extending to the sea; the mass is tolerably

compact, and contains splendid crystals of pyroxene, also labradorite and some olivine; sp. gr. 2·812.

XI. Lava of the eruption of 1852. This lava, collected near the Zafferana mill, is dark grey and compact; sp. gr. 2·809.

XII. Lava of the eruption of 1879 is compact, and of a pale bluish-grey colour; sp. gr. 2·607.

The potash and the comparatively large amount of phosphoric acid present in the lavas, render the soil formed by their weathering exceedingly fertile; the ferric oxide also is of great advantage, both by its physical and chemical properties. This is well seen in the wonderful fertility of the Plain of Mascali, the soil of which is formed of detritus washed down from the disintegrated lava of the Valle dei Bove.

C. E. G.

Mineral and Rock Enclosures in the Basalt of the Persanyer Gebirge. By A. KOCH. **On the Bombs ("Auswürflingé") in the Basalt-tufa from Reps in Transylvania.** By M. SCHUSTER (*Jahrb. f. Min.*, 1879, 660—661).—A. Koch has examined the bombs found in several localities in Transylvania; they have fused surfaces to which basalt ashes adhere. They consist of a crystalline mixture of olivine—in a tolerably fresh condition, omphacite having a cleavage like augite, augite having a conchoidal fracture, and of pyrope in cracked and blood-red particles. The results of Schuster are partially confirmatory and partially supplementary to those of Koch. The bombs are looser and more crumbling the more olivine they contain; on account of its colour and structure, the omphacite of Koch is regarded by Schuster as augite, and he points out the existence of a rhombic pyroxene not mentioned by Koch; it cleaves perfectly parallel to ∞P , and a fracture approximating to $\infty P\infty$ allowed the optical axial angle which lays in $\infty P\infty$ to be measured to $111^{\circ} 58'$; hence it is probably a bronzite rich in iron, but it melts rather easily. Some particles, very hard, pitch-black, and shining, resembling augite, having no distinct cleavage, and in thin section showing themselves grey or greenish and isotropic: these seemed to be spinelle (picotite), since with microcosmic salt they gave no silica skeleton, but a chromium reaction. In one lump hornblende was detected; this has not before been found in the olivine bombs, but often in the augite slag.

H. B.

Examination of the Material of "Vitrified Forts" at Craig Phadrick, Inverness, and Hartmannswillerkopf, Haute Alsace. By DAUBRÉE (*Compt. rend.*, 92, 980—984).—*Craig Phadrick.*—Many fragments resemble very fine-grained granite or leptinite in appearance, but are highly vesicular. The felspar has lost its crystalline character, and the mica has entirely disappeared. The cavities, which occupy at least half the total volume of the rock, are sometimes lined with small crystals. Some of the coarser fragments resemble pegmatite, and felspar can still be distinctly recognised in them. Almost the whole mass of the fine-grained fragments consists of angular grains of quartz cemented together by a vitreous substance apparently produced by the fusion of the felspar. Macled crystals of triclinic felspar, and needles

not macted, of some undetermined substance, can also be distinguished. Other fragments have a much deeper colour, and contain fewer but larger cavities, with brilliant surfaces. The fused mass contains numerous white opalescent grains, consisting for the most part of quartz, and also colourless angular grains of quartz with cavities which appear to have lost their water, arranged in lines. With the latter are associated orthoclase and oligoclase showing every stage of the passage from the crystalline to the vitreous state, the latter being more distinct towards the outside. As in the case of French vitrified forts, many specimens bear impressions of woody structure, in all probability due to the contact of the softened rock with the fuel. Some of the more completely fused, blackish fragments resemble certain lavas in structure. A very abundant vitreous portion contained the following crystals disseminated through the amorphous matter:—Labradorite, often very numerous; pyroxene, elongated, also numerous; humboldtite; octahedra of pleonastic spinelle, very numerous; and crystals resembling enstatite, but differing from the latter by the absence of distinct lines of cleavage.

Hartmannswillerkopf.—The vitrified materials of this locality appear to have been derived from the rock known in Alsace as brown porphyry. The impressions of woody structure are very distinct. Microscopic examination shows that the rock contains the remains of quartz crystals and of felspar, generally orthoclase, but sometimes oligoclase. A dipyrarnidal crystal of quartz which had retained its original form was found in one specimen; imbedded in the more perfectly fused portions are octahedra of spinel, sometimes so ferruginous as to be opaque; humboldtite; oligoclase; and very small yellowish-green rectangular prisms and octahedra, which act on polarised light, and the nature of which has not been determined.

Examination of vitrified forts in different localities shows that the materials of which they are composed have undergone considerable mineralogical changes under the influence of what must have been a very high temperature. Notwithstanding differences in the nature of the original rocks, the products exhibit close analogies. In every case, the intense heat required seems to have been obtained in the same way. It is improbable that the method of producing such very high temperatures was invented independently in distant countries. Probably the knowledge of the process was carried from place to place, and vitrified forts would therefore appear to mark the stopping places of certain migrations. Examination of the material of these forts affords further proof of the ease with which crystalline species are formed in the middle of a vitreous mass heated to a suitable temperature.

C. H. B.

Anomalous Magnetism of the Meteoric Iron at Sainte-Catherine. By J. L. SMITH (*Compt. rend.*, **92**, 843—844).—The meteoric iron at Sainte-Catherine, Brazil, corresponds closely in composition with the thin white metallic plates which are found mixed with the oxides produced by the decomposition of the outer portion of some of the best known masses of meteoric iron. The iron at Sainte-Catherine contains 66 per cent. Fe, and 34 per cent. Ni (Damour):

small plates from Sevier Co., Tennessee, contained 73 per cent. Fe and 27 per cent. Ni (Smith). The unaltered mass of iron at Sevier contains only 6 per cent. Ni. Small fragments of the Sainte-Catherine meteorite are very feebly magnetic, but, if beaten out on an anvil or between sheets of brass, or if heated to incipient redness, they become strongly magnetic. No other substance has been observed to show this peculiar property. The meteorite is more or less polar, and the sulphide which it contains is strongly magnetic. Fragments of the meteorite at Octibbeha, which is exceptionally rich in nickel, containing as much as 60 per cent., do not behave in the same way.

C. H. B.

Nodules of Chromite in Meteoric Iron from Cohahnila. By J. L. SMITH (*Compt. rend.*, **92**, 991—992).—The author has examined various specimens of the meteoric iron from Cohahnila, which he terms "Butcher's meteorites." It is found to be encrusted with arragonite. It contains nodules of troilite intimately associated with a new mineral, daubréelite. In making a new section of the meteoric iron, the author has found a large mass of nodules about 0.6 meter below the surface. It contains no troilite, and an examination with a microscope shows that it is not entirely daubréelite, but contains some translucent particles mostly colourless, but a few of a greenish hue. There are also scales of metallic iron. The author finds the greenish substance to be chromite. The analysis gives 33.82 FeO, 62.61 Cr₂O₃, and small quantities of magnesium, cobalt, and silica. J. I. W.

Organic Chemistry.

Composition of Petroleum from the Caucasus. By P. SCHÜTZENBERGER and N. IONINE (*Compt. rend.*, **91**, 823—825).—An examination of the crude naphtha or petroleum from the Caucasus has shown that a very large portion of the oil, both of high and low boiling points, is formed of hydrocarbons of identical percentage composition, which are isomeric with the olefines, C_nH_{2n} , but sharply distinguished from them by an absence of marked chemical affinities, neither bromine, fuming sulphuric acid, nor fuming nitric acid having any action upon them in the cold. The hydrocarbons were isolated by treating the various fractions first with fuming sulphuric acid and then with nitric acid; they were afterwards washed with an alkaline solution, dried over solid potassium hydroxide, and lastly distilled from sodium. The first fraction began to boil under ordinary pressure at 112° , and the thermometer eventually rose to 230° ; the distillation was then conducted in a partial vacuum of 20 mm., when the distillate came over between 216° and 300° . The analytical numbers obtained from every fraction were almost identical, $C = 86.02$, $H = 14.10$, representing the percentage composition of the first fraction. A closer study of these hydrocarbons has enabled the authors to identify them with the bodies obtained by Wreden in hydrogenising benzene and its

homologues with hydriodic acid. Beilstein and Kurbatow had already arrived at the same conclusion, after an examination of the more volatile portions only of a similar petroleum from the Caucasus; their opinion is therefore confirmed and extended by the present work, it having been shown that not only the light but also the heavy oils possess the same characteristics.

By the action of a bright red heat, these *paraffènes*, as the authors call them, are converted into members of the benzene series, together with naphthalene and anthracene. At a lower temperature, products may be obtained which unite energetically with bromine, and are converted into resinoid polymerides by the action of concentrated sulphuric acid.

When volatilised through a red-hot iron tube, they give an abundant deposit of carbon, which quickly blocks up the tube; the deposit is uniformly impregnated with iron, and is evidently due to the action of the metal upon the hydrocarbon, since this change does not take place when a copper tube is substituted for the iron one.

Only two products of tolerably constant boiling point could be isolated; one at 220—222°, and another between 230° and 232°: the vapour-density of the latter led very nearly to the formula $C_{14}H_{28}$.

J. W.

Action of Palladium, Rhodium, and Platinum on Coal-gas.

By T. WILM (*Ber.*, **14**, 874—879).—The author has studied more closely the curious action of palladium, rhodium, and platinum on coal-gas first observed by Wöhler (*Ber.*, **9**, 1713) in the case of ethylene.

If a current of coal-gas is passed over spongy palladium (reduced from the ammonium palladiochloride), heated over a Bunsen burner in a bulb-tube or small porcelain crucible, a large quantity of carbon is deposited on the inner walls of the crucible or tube, and after a time this collects over the edges of the crucible in cauliflower-like masses. This carbon, on combustion by a stronger heat, does not leave the least trace of palladium, nor does any deposition take place on the metal, which suffers no change of volume during the experiment. This action does not depend on the formation of a compound of carbon and palladium, but is due to the (?) "catalytic" action of the metal, whereby the ethylene is decomposed with deposition of carbon. The action of rhodium on coal-gas is quite different from that of palladium, for under the same circumstances not the slightest deposition of carbon takes place on the sides of the crucible or bulb-tube, as is the case with palladium, but it appears to enter into a loose combination with the rhodium, which is largely increased in volume, and assumes an appearance like tea-leaves, or the chromic oxide obtained by the ignition of ammonium chromate. On admitting air to the tube the contents begin to glow, but do not suffer any diminution in volume; when this has ceased no further combustion of carbon could be observed on passing in a current of air or oxygen. Only after cooling in oxygen and then passing in hydrogen did the glowing recommence, but still without producing any alteration in the volume of the contents of the tube. The volume left after the above treatment was

equal to three or four times that of the original metal, and was free from carbon. The composition of the mass left after the action of the coal-gas approximates to the formula RhC .

The action of platinum on coal-gas differs from that of palladium on the one hand, and of rhodium on the other. Only after a long time can any deposition of carbon be observed, which then takes place on the margin of the platinum, whilst the middle maintains its grey metallic appearance, nor does any alteration in volume occur. When the action had gone on for an hour and a half, the weight of the metal had increased by 3.28 per cent., the formula PtC requiring 5.7 per cent. C. On exposure to the air, the contents of the vessel underwent no change, but on passing a current of air over the heated mass, the carbon was completely burnt.

Platinum, therefore, appears to produce a separation of carbon by contact action, as in the case of palladium, but, unlike the latter, the carbon is deposited in the pores of the metal without changing its volume, and not on the surrounding walls of the crucible, whilst rhodium forms a loose combination with the element.

These results have, undoubtedly, an important bearing on the manufacture of platinum vessels, and appear to account for the fact, which has been frequently observed, of vessels giving way under circumstances which would be otherwise inexplicable, the effect in these cases being probably due to the presence of rhodium.

T. C.

Action of Molecular Silver on Carbon Chlorides. By H. GOLDSCHMIDT (*Ber.*, 14, 927—930).—Carbon tetrachloride is decomposed by molecular silver at 200° , forming hexachlorethane, C_2Cl_6 . Heated at 250° with an excess of water, it is split up into hydrochloric acid and carbonic anhydride, but if only a small quantity of water is taken, carbonyl chloride is produced.

Hexachlorethane is converted into tetrachlorethylene by the action of molecular silver at 280° .

From these results, the author infers that the four affinities by which the chlorine is united to the carbon-atom in carbon tetrachloride, are not equal.

W. C. W.

Double Platinocyanides. By R. SCHOLTZ (*Wien. Akad. Ber.*, 82 [2], 1233—1240).—The author has prepared and made crystallographic measurements of several double platinocyanides.

Hydroxylamine platinocyanide, $PtCy_2.(NH_3.OH.CN)_2 + 2H_2O$, crystallises in dark orange, prismatic crystals, which deliquesce rapidly in the air. The crystals exhibit a blue fluorescence, and, on heating, are decomposed with formation of platinum cyanide.

Ethylamine platinocyanide, $PtCy_2.(NH_3Et.CN)_2$, forms large colourless deliquescent crystals belonging to the tetragonal system with axial ratio $a : a : c = 1 : 1 : 0.7738$. This substance is soluble in water and alcohol.

Diethylamine platinocyanide, $PtCy_2.(NH_2Et_2.CN)_2$, forms colourless crystals of the triclinic system with axial ratio $a : b : c = 1.75 : 1 : 1.39$.

Triethylamine platinocyanide, $PtCy_2.(NHEt_3.CN)_2$, forms colourless

glistening monoclinic crystals, with axial ratio $a : b : c = 1.8014 : 1 : 0.8959$.

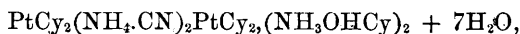
Triethylamine platinocyanide, $\text{PtCy}_2(\text{NHEt}_3.\text{CN})_2$, crystallises in colourless glistening crystals (m. p. 80°) of the monoclinic system, with axial ratio $a : b : c = 1.8014 : 1 : 0.8959$.

Aniline platinocyanide, $\text{PtCy}_2(\text{NH}_3\text{Ph.CN})_2$, forms pearly leaflets, easily soluble in water. On heating it is decomposed, at first with separation of aniline, and finally leaving only a residue of platinum. The crystals are in the triclinic system, with axial ratio $a : b : c = 1.33 : 1 : 1.25$.

Paratoluidene platinocyanide, $\text{PtCy}_2(\text{NH}_3\text{C}_7\text{H}_7.\text{CN})_2$, crystallises in rosy cuneiform crystals of the monoclinic system, with axial ratio $a : b : c = 0.6382 : 1 : 0.4465$.

α -*Naphthylamine platinocyanide*, $\text{PtCy}_2(\text{NH}_3\text{C}_{10}\text{H}_7.\text{CN})_2$, forms greyish glassy crystals of the rhombic system, with axial ratio $a : b : c = 0.5112 : 1 : 1.2033$.

Ammonium hydroxylamine platinocyanide,



forms golden prismatic crystals, possessing a copper-like lustre.

Lithium hydroxylamine platinocyanide,



forms purple-red, prismatic hygroscopic needles with an emerald-like metallic lustre.

V. H. V.

Action of Ammonium Chloride on Glycerol. By A. ÉTARD (*Compt. rend.*, **92**, 795—797).—The crude products of the distillation of glycerol with ammonium chloride have a strongly acid reaction. When they are mixed with dilute sulphuric acid, distilled with water, and the aqueous distillate is extracted with ether, a chlorinated compound is obtained, which boils at 175° . The acids accompanying this product decompose potassium carbonate with effervescence, but the salts formed have not been isolated. On evaporation, their solution is decomposed, with formation of compounds which attack the eyes like acrolein. Complete analyses of the alkaloid previously described, which the author proposes provisionally to name *glycoline*, prove that its formula is $\text{C}_6\text{H}_{10}\text{N}_2$, and not $\text{C}_6\text{H}_9\text{NO}$, as at first supposed. The platinochloride and aurochloride have the composition $\text{C}_6\text{H}_{10}\text{N}_2.2\text{HCl}, \text{PtCl}_4$ and $\text{C}_6\text{H}_{10}\text{N}_2.\text{AuCl}_3$ respectively. The hydrochloride, $\text{C}_6\text{H}_{11}\text{N}_2\text{Cl}$, is obtained in small mammillary groups of needles, when its aqueous solution is evaporated over sulphuric acid. It is very soluble in water and alcohol, but the crystals do not deliquesce except in a very moist atmosphere. By heating glycoline with an excess of ethyl iodide at 100° for about an hour, an ethiodide, $\text{C}_6\text{H}_{10}\text{N}_2.\text{EtI}$, is obtained in lemon-coloured needles, unaltered when exposed to the air, and only slightly soluble in ether, but extremely soluble in alcohol. Apparently sodium nitrite is without action on the acid sulphate of glycoline; hence the latter cannot be regarded as containing the group NH_2 . When treated with nitric acid, glycoline, as previously stated, is entirely converted into carbonic anhydride and

hydrocyanic acid, but oxidation with permanganic acid appears to proceed more regularly.
C. H. B.

Rotatory Power of Carbon Compounds. By T. THOMSEN (*Ber.*, 14, 807—808).—This is a reply to Landolt's criticism (this vol., 403) on former publications (*ibid.*, 215) by the author, in which it is shown that Landolt has entirely overlooked the chemical side of the question.
P. P. B.

Acetic Derivatives of Cellulose. By FRANCHIMONT (*Compt. rend.*, 92, 1053—1054).—On treating cellulose (Swedish filter-paper) with acetic anhydride and sulphuric acid, the author has obtained two bodies in addition to the crystalline derivatives already described by him. The first is a white powder (m. p. 232°), which dissolves readily in amyl alcohol: with hot baryta-water it gives a white precipitate, insoluble in acids and alkalis, but soluble in ammoniacal copper solution. It is found to contain—C (1) 49.12, (2) 49.21 per cent., H 5.57 per cent., acetic acid (1) 62.2, (2) 62.5 per cent. The author assigns no formula to the substance.

The second body is insoluble in amyl alcohol, but dissolves in boiling acetic acid, from which solution it is precipitated as a jelly on adding water. Its melting point is indefinite, and it blackens at a high temperature.
J. I. W.

Ethyl Peroxide. By BERTHELOT (*Compt. rend.*, 92, 895—897).—Ethyl peroxide is obtained by passing a slow current of perfectly dry and strongly ozonised oxygen over anhydrous ether. The ozone is gradually, although incompletely, absorbed, and a dense syrupy liquid is formed, which becomes viscous, but does not solidify at -40° . When heated it distils partially, but finally decomposes with a violent explosion. It is dissolved by water, and is at the same time decomposed into alcohol and hydrogen peroxide. The aqueous solution behaves with potassium permanganate and dichromate and other reagents, like a solution of hydrogen peroxide. Estimation of the amount of hydrogen peroxide formed by its decomposition showed that the composition of ethyl peroxide is Et_4O_3 . The reaction with water may be represented by the equation $\text{Et}_4\text{O}_3 + 3\text{H}_2\text{O} = 4\text{EtHO} + \text{H}_2\text{O}_2$. This production of ethyl peroxide by the direct action of ozone furnishes a method of preparing hydrogen peroxide by means of the latter.
C. H. B.

Action of Phosphorus Pentachloride on Isobutaldehyde. By S. ECONOMIDÉS (*Compt. rend.*, 92, 884—886).—The action of phosphorus pentachloride on isobutaldehyde at ordinary temperatures gives rise to monochlorisobutylene and isobutylene dichloride, the latter being formed in larger quantity. *Monochlorisobutylene*, $\text{Me}_2\text{C}:\text{CHCl}$, is a limpid colourless liquid, with an agreeable odour; sp. gr. at 12° = 0.9785; b. p. = $66-70^{\circ}$; vapour density, 89.7. The same compound is formed in small quantity when dichlorisobutylene is treated with alcoholic potash. The liquid thus obtained has an odour resembling that of fennel, and somewhat different from that of

the monochlorisobutylene. *Isobutylene dichloride*, $C_4H_8Cl_2$, is a colourless liquid, with an agreeable odour; b. p. $103-105^\circ$; sp. gr. at $12^\circ = 1.0111$; vapour density, 127. It cannot be distilled without partial decomposition. When this compound is heated at 180° with twice its weight of aqueous ammonia, there is formed, together with other chlorinated compounds, pure monochlorisobutylene boiling at $65-68^\circ$, and having an odour of fennel. When exposed to moist air, it deposits a white crystalline substance. The action of aqueous or alcoholic ammonia on the isobutylene dichloride also gives rise to certain bases not yet isolated.

C. H. B.

Condensation-products of Aldehydes and their Derivatives.

By A. LIEBEN and S. ZIESEL (*Wien. Akad. Ber.* [2], **82**, 960—981).—*Crotonaldehyde and its derivatives* (see also this Journal, **36**, 615).—The crotonaldehyde used in these experiments was prepared by heating 1 vol. of a concentrated solution of sodium acetate with about 10 vols. of aldehyde in a sealed tube for 24 hours at 100° , and separating the crotonaldehyde by fractional distillation. On warming with a concentrated solution of sodium hydrogen sulphite, crotonaldehyde dissolves, and on cooling a crystalline magma of the sulphite compound is formed, but the aldehyde cannot be separated from this by distilling with sodium carbonate. The acrolein compound behaves in a similar manner; this peculiarity is to be investigated.

Crotonaldehyde combines directly with two atoms of bromine, forming a heavy oil, which neither distils without decomposition, nor solidifies even when cooled to -35° , and on standing turns dark and evolves hydrobromic acid. It forms a bisulphite, thus showing an aldehyde character, and is perhaps dibromobutaldehyde. Of several methods tried for the reduction of crotonaldehyde, digestion with acetic acid and iron filings was found to be the best. On distillation, an oil is obtained, which consists of normal butyraldehyde, normal butyl alcohol, and crotonyl alcohol. The aldehyde may be removed by treatment with hydrogen sodium sulphite, and the two alcohols separated by means of bromine, which leaves the butyl alcohol unattacked. By distilling under 50 mm. pressure, the butyl alcohol passes over at 56° . The crotonyl alcohol is separated with greater difficulty. The brominated compound left in the residue is treated with sodium-amalgam in presence of water, then distilled, digested with potash and lime, and repeatedly distilled over sodium. The crotonyl alcohol thus obtained contains about 10 per cent. of butyl alcohol (b. p. $117.5-120^\circ$); its odour somewhat resembles that of allyl alcohol, but is not so unpleasant; it combines readily with bromine.

The alcohol mixture contains about 88.36 per cent. crotonyl alcohol. By the action of hydriodic acid or iodine and phosphorus on the mixture of alcohols (boiling at 117°) at the ordinary temperature of the air, a product boiling at $124-129^\circ$ is obtained, which is shown, by V. Meyer's reaction, to be a mixture of normal and secondary butyl iodide; the latter is the product of the action of hydriodic acid on crotonyl alcohol. By boiling the above-mentioned brominated mixture with excess of water, then distilling off about two-thirds of the whole to get rid of butyl alcohol and an aldehyde, and treating with lead

oxide to remove hydrobromic acid, a liquid is obtained, which, on evaporating, leaves butenylglycerol as a thick yellow liquid. It has a sweet taste, distils at $172\text{--}175^\circ$ (uncorr.) under 27 mm., with slight decomposition; it does not crystallise, and, in a freezing mixture of solid carbonic anhydride and ether, turns to a vitreous mass. Its triacetin, $\text{C}_4\text{H}_7(\text{AcO})_3$, made by heating the glycerol with acetic anhydride at 150° for 20 hours, distils at $153\text{--}155^\circ$ (uncorr.) under 27 mm., and boils under 740.2 mm. at 261.8° (corr.); it is a thick, colourless liquid, not miscible with water, with a feeble but pleasant odour. On treating the glycerol with fuming hydriodic acid, even in the cold, iodine separates out, and by digesting for 6 hours at 100° in a sealed tube, secondary butyl iodide is formed, whilst with phosphorus and iodine it yields crotonyl iodide, a yellow oil (b. p. $131\text{--}133^\circ$), with odour somewhat like allyl iodide. On shaking with mercury it yields a body, crystallising from absolute alcohol in white crystals, which very quickly turn yellow. This butenylglycerol, when heated to about 255° with oxalic acid containing 0.5 per cent. of both ammonium and sodium chlorides, employing Tollens' method, yields crotonyl alcohol along with carbonic oxide and formic acid.

D. A. L.

Preparation of Isobutylal. By S. ECONOMIDÉS (*Compt. rend.*, 92, 886).—A current of hydrochloric acid gas is passed through a well-cooled mixture of equal parts of isobutaldehyde and absolute alcohol. The upper layer of liquid which separates out is washed with water, dried over potassium carbonate, and heated with sodium ethylate until no more sodium chloride is formed. The isobutylal is then separated by addition of water. It is a colourless liquid (b. p. $134\text{--}136^\circ$), with an odour recalling that of essence of fennel. Sp. gr. at $12.4 = 0.9957$; vapour density, 143.5.

C. H. B.

Production of Crotonyl Chloral. By A. LIEBEN and S. ZIESEL (*Wien. Akad. Ber.* [2], 82, 982—985).—The method of reduction mentioned on p. 710 is employed in this case also, the quantities used being 1 part crotonyl chloral, 4 parts iron filings, and 8 parts of 50 per cent. acetic acid. With exception of a small quantity of a body boiling at $157\text{--}160^\circ$, and containing 28.02 per cent. chlorine, the products are the same, namely, normal butyl alcohol, crotonyl alcohol, and normal butaldehyde. Sarnow (*Annalen*, 164, 93), by a partial reduction of crotonyl chloral, obtained monochlorcrotonaldehyde and crotonyl alcohol.

D. A. L.

Formation of Acetone and Thiacetone. By W. SPRING (*Ber.*, 14, 758—760).—Propidene dichloride, CCl_2Me_2 , when heated with silver acetate and alcohol in sealed vessels at 100° , yields acetone, acetic anhydride, and silver chloride. This dichloride is decomposed by sodium thioacetate in a similar manner, yielding sodium chloride and a thiabetic ether, $\text{CMe}_2(\text{AcS})_2$. The latter yields thiacetone when heated.

P. P. B.

New Method of Brominating Organic Acids. By C. HELL (*Ber.*, 14, 891—893).—This consists in first converting the acid into

its anhydride or bromide, which are very much more easily brominated than the acid itself, and then submitting these to the action of bromine.

T. C.

Compound of Calcium Chloride with the Fatty Acids. By A. LIEBEN (*Wien. Akad. Ber.*, **82**, [2], 1255—1283).—The author and G. Janecek (*Annalen*, **187**, 132) have already indicated the existence of crystalline compounds of calcium chloride with several of the fatty acids. In the present research, he has investigated the combinations of calcium chloride, butyric acid, and water, the nature of which depends on the condition of the experiment. Allusion is also made to the readiness with which the compounds decompose, whether by heat, or by absorption of moisture when exposed even for a short time to the air. In order to purify the crystals from the mother-liquors it was found necessary to wash them with dry butyric acid, and to dry them on a porous plate over sulphuric acid.

Compound of Butyric Acid, Calcium Chloride, and Water.—On the addition of a few drops of water to a saturated solution of calcium chloride in butyric acid, a white voluminous precipitate is thrown down which after some time assumes a crystalline form. The compound after purification has the composition $\text{CaCl}_2 + 2\text{C}_4\text{H}_8\text{O}_2 + 2\text{H}_2\text{O}$.

Compound of Butyric Acid, Calcium Chloride, and Butyrate.—On evaporating a saturated solution of calcium chloride in butyric acid in a vacuum, crystalline needles separate out having the composition—



the sides of the flask are at the same time covered with a milk-white efflorescence of the compound. The author does not consider that the formation of calcium butyrate is due to an impurity of lime in the calcium chloride, but to the decomposition of the calcium chloride. When this dissolves in the butyric acid, incipient decomposition ensues, with liberation of hydrochloric acid, which remains dissolved in the butyric acid, and prevents the action going further until it is removed by boiling the solution or evaporating it over lime.

Compound of Calcium Chloride with Butyric Acid.—The crystals of $\text{CaCl}_2 + 2\text{C}_4\text{H}_8\text{O}_2 + 2\text{H}_2\text{O}$, obtained by the process mentioned above, when kept for several months over sulphuric acid, lose all their water and part of the butyric acid. They are thus converted into a fine delicate milk-white powder of composition $\text{CaCl}_2 + \text{C}_4\text{H}_8\text{O}_2$.

The probable existence of a whole series of such compounds is pointed out by the author.

V. H. V.

β -Iodolactic Acid. By MELIKOFF (*Ber.*, **14**, 937—939).—Hydriodic acid, like hydrochloric and hydrobromic acids, combines directly with glycidic acid. In this case, β -iodolactic acid is formed. This acid crystallises in transparent prisms, freely soluble in water, alcohol, and ether. β -Iodolactic acid melts at 101° ; the chloro- and bromo-lactic acids melt at 79° and 90° respectively. Alcoholic potash converts β -iodolactic acid into glycidic acid. Zinc β -iodolactate forms a crystalline powder; the calcium salt is amorphous and the silver salt is very unstable.

Zinc glycidate, $\text{Zn}(\text{C}_3\text{H}_2\text{O}_3)_2 + \text{H}_2\text{O}$, is amorphous; ammonium glycidate can be obtained in prismatic crystals which are easily soluble in water. W. C. W.

Amido-acids derived from Iso-hydroxyvaleric Acid. By E. DUVILLIER (*Ann. Chim. Phys.* [5], **21**, 433—448).—The methyl, ethyl, and phenyl amido-derivatives of hydroxybutyric acid have been already described: in the present paper the author gives the details of his work on iso-hydroxyvaleric acid.

Methylamidovaleric acid, $\text{CHMe}_2\text{CH}(\text{NHMe}).\text{COOH}$, was obtained by adding a pure concentrated solution of methylamine to bromovaleric acid. It is a crystalline substance, soluble in water and alcohol, but insoluble in ether. It is neutral to litmus, and has a slightly sweet taste. The pure acid may be heated to 120° without alteration, but at a higher temperature it sublimes without melting or blackening; it nevertheless undergoes at the same time a partial decomposition.

The sulphate, hydrochloride, platinochloride, and aurochloride were prepared and analysed; they present no characteristics requiring special mention.

Ethylamidovaleric acid, $\text{CHMe}_2\text{CH}(\text{NHet}).\text{COOH}$, and its salts were prepared by the use of ethylamine, in the same manner as the methyl-derivatives: they resemble the latter so closely that it is practically impossible to distinguish between them, except by ultimate analysis.

By the action of an ethereal solution of aniline on bromovaleric acid, *phenylamidovaleric acid* was obtained, $\text{CHMe}_2\text{CH}(\text{NHPh}).\text{COOH}$. The mixture requires to be heated in an oil-bath at 130° , after which it is washed with water to remove the aniline hydrobromide which is formed. The amido-acid occurs as a viscid mass, insoluble in cold water, but which by crystallisation from boiling water can be obtained in the form of brilliant colourless needles, becoming brown by exposure to light. Heated above 110° , it first melts and finally sublimes with partial decomposition.

It may be distinguished from its methyl and ethyl analogues by the fact that its aqueous solution reduces solutions of silver and mercurous nitrates. Phenylamidovaleric acid dissolves easily in dilute hydrochloric acid, and the solution when evaporated in a vacuum deposits crystals of the hydrochloride in radiated mammillary groups. The hydrochloride is anhydrous, soluble in water and alcohol, but insoluble in ether. J. W.

Iron Oxalates and some of their Double Salts. By J. M. EDER and E. VALENTA (*Wien. Akad. Ber.*, **82**, 614—627).—*Ferric oxalate* in solution was found to have the constitution $\text{Fe}_2(\text{C}_2\text{O}_4)_3$. It may be prepared by digesting freshly precipitated ferric hydrate with oxalic acid, light being excluded. It forms a greenish-yellow solution, in which alcohol does not cause a precipitate. It cannot be obtained in a crystalline form.

Basic Ferric Oxalates.—On mixing solutions of ferric salts and ammonium oxalate, a red-brown precipitate was obtained, especially on

adding alcohol, after repeated washings with which, and drying at 100° , it has the composition $\text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{Fe}_2(\text{OH})_6 + 4\text{H}_2\text{O}$. This oxalate when heated with water, gives up oxalic acid, and yields $\text{Fe}_2(\text{C}_2\text{O}_4)_3 + 9\text{Fe}_2(\text{OH})_6$.

Normal *potassium ferric oxalate*, $\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{K}_6 + 6\text{H}_2\text{O}$, agrees in properties with the salt described by Busz. A potassium ferric oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{K}_4 \cdot 5\text{H}_2\text{O}$, of an olive-brown colour, seems to have the same relation to the above green salt as the red chromium potassium oxalate to the green one.

Normal *sodium ferric oxalate* has the composition $\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{Na}_6 + 11\text{H}_2\text{O}$, and normal *ammonium ferric oxalate*, $\text{Fe}_2(\text{C}_2\text{O}_4)_3(\text{NH}_4)_6 + 8\text{H}_2\text{O}$, forms bright green crystals permanent in the air.

Ferrous oxalate is permanent in the air even when in a moist condition, but is very rapidly oxidised in the presence of alkalis. It is soluble in 5,000 parts of water at 15° , but is soluble in 29 parts of a 14 per cent. solution of ferric oxalate at 15°C . *Potassium ferrous oxalate*, $\text{Fe}(\text{C}_2\text{O}_4)_2\text{K}_2 + \text{H}_2\text{O}$, form small golden-yellow crystals almost permanent in the air when dry, but oxidising rapidly in a moist condition. *Ammonium ferrous oxalate*, $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{NH}_4)_2 + 3\text{H}_2\text{O}$, is very similar to the potassium salt.

It is partially decomposed by water.

A corresponding sodium salt has not yet been obtained in a pure state, sodium oxalate separating on crystallising. W. R. H.

Tartronic Acid. By C. BÖTTINGER (*Ber.*, **14**, 729—730).—Tartronic acid is obtained from glyoxylic acid in the same manner as oxyethylidenesuccinic acid is from pyrroacemic acid (*Ber.*, **14**, 87, and this vol., 234), viz., by treating finely powdered potassium cyanide with glyoxylic acid and boiling the product with baryta water. A mixture of barium carbonate and tartronate is thus formed, from which tartronic acid is obtained by decomposing it with sulphuric acid. The author finds the melting point to be 183° and not 175° , as is usually stated, and regards it as probable that by heat the tartronic acid is first converted into glycollide, which melts at 180° .

P. P. B.

Action of Zinc Ethyl on Ethyl Tartrate. By E. MULDER and H. G. L. v. DER MEULEN (*Ber.*, **14**, 918—919).—If ethyl tartrate is slowly added to zinc ethyl diluted with absolute ether, a gelatinous mass is produced, which when dried, forms a white amorphous powder

of the composition $\text{Zn} \begin{cases} \text{O.CH.COOEt} \\ | \\ \text{O.CH.COOEt} \end{cases}$

W. C. W.

Tanatar's Trioxymaleic Acid. By A. KÉKULÉ and R. ANSCHÜTZ (*Ber.*, **14**, 713—717).—This acid which Tanatar obtains by the oxidation of maleic acid, the authors show, from the properties of its calcium salt, to be inactive tartaric acid.

P. P. B.

Derivatives of Pyromucic Acid. By O. WALLACH (*Ber.*, **14**, 751—754).—Pyromucamide ($\text{C}_4\text{H}_3\text{O}$). CONH_2 (m. p. 140 — 142°), like benzamide, is converted by phosphorus pentachloride into the correspond-

ing nitril, viz., *furfuronitril* (C_4H_3O).CN, a colourless liquid (b. p. $146-148^\circ$), turning brown on exposure to the air. It is converted into a base by nascent hydrogen, probably furfonylamine.

Pyromucethylamide (C_4H_3O).CO.NHEt, obtained by the action of ethylamine on ethyl pyromucate is a thick, mobile, colourless oil (b. p. 258°). Phosphorus pentachloride converts it into a crystalline chloride (C_4H_3O).CCl₃.NHEt, which is volatile with but slight decomposition.

Ethylamine pyromucate when distilled with phosphorus pentachloride yields *pyromucyl chloride*, a pungent smelling liquid (b. p. $160-180^\circ$). On treating the residue with potassium hydroxide, it yields a base boiling above 200° , the platinochloride of which has the formula $[C_9H_{14}N_2(OH)Cl]_2PtCl_4$, and hence the base is an amidine having the formula (C_4H_3O).CNEt.NHEt.

Analysis of Platinum Salts.—To determine the platinum and chlorine in such a salt, the salt is evaporated in a water-bath with a concentrated solution of sodium ethylate representing 1 gram of sodium. It is further heated by a naked flame, and the alcohol ignited and allowed to burn. After the flame is extinguished, the heating is continued and a residue obtained consisting of sodium carbonate and chloride, platinum and carbon. When cold, the chlorine and platinum are determined in this by the usual methods. P. P. B.

A Compound of Thiocyanacetic Acid and Carbaminthioglycollic Acid. By P. CLAESSON (*Ber.*, **14**, 731—732).—Thiocyanacetic acid in presence of a small quantity of water is converted into a solid, which was formerly regarded as a polymeride (*Ber.*, **10**, 1346). This substance, however, proves to be a compound of thiocyanacetic acid and carbaminthioglycollic acid, and to it the author attributes the following constitution: $NH : C < \begin{matrix} S.CH_2.COOH \\ NH.COS.CH_2.COOH \end{matrix}$, and is therefore carbamido-carbamindithioglycollic acid. Its constitution is similar to Nencki and Jäger's phenylcarbodiimidothioglycollic acid (*J. pr. Chem.* [2], **16**, 17). It is soluble in hot water, and insoluble in cold. By boiling with hydrochloric acid it is resolved into thioglycollic acid, carbonic anhydride, and ammonia. It melts and decomposes at 149° . It reacts with alkaline carbonates forming carbaminthioglycollic acid, and with metallic salts yields metallic thioglycollates, carbonic anhydride and ammonia, as do both thiocyanacetic and carbaminthioglycollic acids. P. P. B.

Thiocyanuracetic Acid. By P. CLAESSON (*Ber.*, **14**, 732—734).—On distilling ethyl thiocyanacetate it is decomposed, and from the residue Heintz (*Annalen*, **136**, 223) obtained a crystalline compound, which is a polymeride of ethyl thiocyanacetate, and is styled by the author ethyl thiocyanuracetate. It crystallises from ether in beautiful needles (m. p. 81°); it is converted by alcoholic potash into the potassium salt, which is easily soluble in water, but insoluble in alcohol and concentrated potassium hydroxide.

Thiocyanuracetic acid is obtained by acidifying the solution of the potassium salt; it crystallises in needles (m. p. 199.5°), which are

soluble in alcohol and ether. The salts with the exception of those of the alkali metals are insoluble or only sparingly soluble. It is a tribasic acid. The neutral barium salt obtained by adding barium chloride to a solution of the potassium salt, crystallises in sparingly soluble prisms, containing 6 mols. H_2O . The di-acid barium salt is obtained by heating a mixture of barium chloride and potassium thiocyanurate with acetic acid; it crystallises in large prisms containing 2 mols. H_2O . When thiocyanuracetic acid is heated with hydrochloric acid, it is resolved into cyanuric and thioglycollic acids.

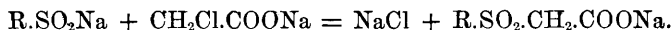
Amongst the products of the decomposition of ethyl thiocyanacetate, the following have been found: alcohol, ether, carbon bisulphide, ethyl thioglycollate, thiocyanacetyl, ethylcarbylamine, and cyanogen gas.

P. P. B.

Action of Sulphuric Acid on Acetic Anhydride. By FRANCHIMONT (*Compt. rend.*, **92**, 1054—1056).—When acetic anhydride and sulphuric acid are mixed in molecular proportions, and the mixture, after remaining at rest for some time is heated to 130° , and when cold dissolved in water, almost the whole of the sulphuric acid enters into combination with the acetic anhydride, and forms sulphacetic acid. The author states that it appears as if an acetylsulphuric acid were first formed and this, on treatment with water, decomposed, with formation of sulphacetic acid. He proposes further to investigate the matter.

J. I. W.

Sulphonacetic Acids. By S. GABRIEL (*Ber.*, **14**, 833—834).—The synthesis of these acids can be effected by acting on sodium chloracetate with the sodium salt of a sulphinic acid, thus:



The fact that the acids so obtained are identical with those formed by the oxidation of thioacetic acids, confirms Otto's views of the constitution of the sulphinic acids (this Journal, 1880, 810).

Phenylsulphonacetic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{COOH}$, is obtained by dissolving 1 mol. benzenesulphinic acid and 1 mol. of chloracetic acid in water, neutralising with potassium hydroxide and heating the resulting liquid; after the separation of sodium chloride, the syrupy mass is evaporated to dryness on a water-bath. The free acid is obtained by decomposing the sodium salt with hydrochloric acid, and extracting with ether. The acid is easily soluble in alcohol and ether, and crystallises from hot benzene in colourless needles (m. p. $110-111^\circ$). It is identical with the acid obtained by Claesson by oxidising phenylthioacetic acid.

Paratoluenesulphonacetic acid, $\text{C}_7\text{H}_7\text{SO}_2\text{CH}_2\text{COOH}$, is prepared in a similar manner from paratoluenesulphinic acid. It is sparingly soluble in hot water, and crystallises from benzene in small crystals (m. p. $117-118.5^\circ$). Its silver salt is obtained in shining, rhombic tablets by adding silver nitrate to the solution of its ammonium salt.

P. P. B.

Action of Sulphuryl Chloride on Dimethylamine. By R. BEHREND (*Ber.*, **14**, 722—723).—A cold solution of dimethylamine in

chloroform reacts with a similar solution of sulphuric dichloride, producing tetramethylsulphamide, as follows :—



Tetramethylsulphamide is sparingly soluble in water, but soluble in alcohol, ether, and benzene; it crystallises from alcohol in colourless well-formed tablets (m. p. 73°), and may be sublimed without decomposition. When it is boiled with potassium hydroxide, the tetramethylsulphamide decomposes with evolution of dimethylamine.

Sulphuric dichloride reacts on the amido-bases of the aromatic series, producing chloro-substitution products. P. P. B.

Phosphorus Betaines. By E. A. LETTS (*Proc. Roy. Soc. Edin.*, **11**, 40—46).—The researches were instituted to determine whether the compounds of thetine would show greater analogies to the phosphobetaines than to the compounds of betaine itself.

The action of chloroacetic acid on triethylphosphine forms triethylphosphobetaine, $\text{PEt}_3\text{Cl}\cdot\text{CH}_2\text{COOH}$, which is not deliquescent; it has an acid reaction, and forms a well-defined platinumchloride, sulphate, and base. The anhydrous base is obtained by exposure in a vacuum for some months.

Ethyl chloracetate and triethylphosphine form a brown syrup; the platinumchloride has the composition $(\text{C}_6\text{H}_{17}\text{PO}_3\text{EtCl})_2\cdot\text{PtCl}_4$, and this ethylchloride of triethylphosphobetaine is decomposed by silver oxide, the anhydrous base before referred to being produced. The ethylbromide and ethiodide have also been prepared; the compounds of phosphobetaine like the oxy-salts of dimethylthetine, yield carbonic anhydride when heated. The experiments described prove a close analogy to exist between the compounds of phosphobetaine and of thetine; but these analogies do not exist between these two substances and the corresponding nitrogen compound betaine, for the salts of the latter when heated, either volatilise unchanged, or dissociate into trimethylamine and a derivative of acetic acid.

E. W. P.

Substituted Oxamides, Formamides, and Diethyloxamic Acid. By O. WALLACH (*Ber.*, **14**, 735—751).—Former experiments have shown that the amides of oxalic acid are easily converted into bases, by the action of phosphorus pentachloride; the following is an account of the preparation of di-substituted oxamides and the products obtained from them by the action of phosphorus pentachloride.

Isodiethyl oxamide, $\text{Et}_2\text{N}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, obtained by the action of ammonia on ethylic diethyloxamate (b. p. 253 — 254°), crystallises in well-formed transparent crystals (m. p. 126° , b. p. 266 — 268°), and sublimes at 100° . Phosphorus pentachloride acts on this body, and the resinous product yields the base chloroxyethylene, $\text{C}_6\text{H}_5\text{ClN}$, which is also obtained from the symmetrical diethyloxamide $(\text{CO}\cdot\text{NH}\text{Et})_2$. (*This Journal*, 1877, **11**, 184.)

Diethylcarbamine cyanide, $\text{CN}\cdot\text{CO}\cdot\text{NEt}_2$, is obtained by heating isodiethyloxamide with phosphoric anhydride; it is a colourless liquid (b. p. 219 — 220°), lighter than water, volatile in steam. By the action of phosphorus pentachloride, it is also converted into chlor-

oxaethylene. Its formation is explained as follows: The first product is the chloride $\text{CN.CCl}_2.\text{NEt}_2$, which when heated loses ethyl chloride, and is converted into $\text{CN.CCl}:\text{NEt}$, with which the ethyl chloride unites to form $(\text{CCl}:\text{NEt})_2$; by the action of heat, this is converted into chloroxaethylene and hydrochloric acid. The formation of this base from iso-diethyloxamide is now easily understood, inasmuch as the first product, viz., $\text{NH}_2.\text{CCl}_2.\text{CCl}_2.\text{NEt}_2$, would, by loss of hydrochloric acid, be converted into the chloride of diethylcarbamine cyanide. It would thus appear that the unsymmetrical di-substituted oxamides are not likely to yield any clue to the formation of bases from the oxamides.

Diphenyloxamide, $(\text{CO.NHPh})_2$, is converted by phosphorus pentachloride into a chloride which forms a thio-compound with sulphuretted hydrogen (this Journal, **36**, 784; **38**, 556); when heated, it yields no base, a fact attributed to the presence of two aromatic nuclei.

Ethylphenyloxamide, EtHN.CO.CO.NHPh , is converted into a chloride by the action of phosphorus pentachloride. The chloride is converted by sulphuretted hydrogen into a thiamide, NHEt.CS.CS.NHPh , which crystallises in red tabular crystals (m. p. $36-37^\circ$), and is soluble in ether and chloroform. When heated by itself, the chloride loses hydrochloric acid and is converted into a base, $\text{C}_{10}\text{H}_9\text{ClN}$.

Monethyloxamide and *monophenyloxamide* do not yield bases when treated with phosphorus pentachloride.

Triethyloxamide, NHEt.CO.CO.NEt_2 , is obtained by the action of aqueous ethylamine on ethyl diethyloxamate; it is a liquid miscible with water, volatile in steam, and boiling at $257-259^\circ$; phosphorus pentachloride converts it into resinous products.

Attempts to prepare tetrethylloxamide by the action of diethylamine on ethylic diethyloxamate, and by the action of heat on the salt of diethylamine and diethyloxamic acid, led to negative results.

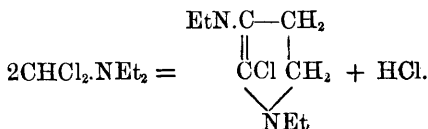
For the preparation of diethyloxamic acid, the author recommends that instead of decomposing ethyl diethyloxamate with potassium hydroxide, as recommended by Heintz (*Annalen*, **127**, 53), a solution of sodium ethylate should be employed. The author finds that diethyloxamic acid melts at $99-101^\circ$, and not at 80° , as stated by Heintz (*loc. cit.*).

Diethylamine diethyloxamate, $\text{NEt}_2.\text{CO.COONH}_2\text{Et}_2$, is obtained by dissolving diethyloxamic acid in diethylamine, or by mixing the alcoholic solutions of these compounds. It is decomposed by dry distillation into diethylamine and *diethylformamide*, HCO.NEt_2 . Since diethyloxamic acid when heated above its melting point is resolved into carbonic anhydride and diethylformamide, the formation of the latter compound in the above case is explained by the dissociation of the salt into diethylamine and diethyloxamic acid, which latter is converted into diethylformamide, thus: $\text{NEt}_2.\text{CO.COOH} = \text{HCO.NEt}_2 + \text{CO}_2$.

The author confirms Linnemann's observations (*Chem. Centr.*, 1880, 139), regarding the properties of diethylformamide; further, it is observed that this compound has basic properties; a platinumchloride, $[\text{HCO.NEt}_2\text{HCl}]_2.\text{PtCl}_4$, was obtained, by adding platinum chloride to the solution obtained by passing hydrochloric acid gas into the ethereal solution of the formamide.

Chloride of diethyloxamic acid, $\text{NEt}_2\text{CO}\cdot\text{COCl}$, is formed when phosphorus pentachloride reacts with diethyloxamic acid at low temperatures. Its existence is shown by the fact that when the product of the reaction is dissolved in ether and treated with ammonia, isodiethyloxamide is obtained. Attempts to prepare tetraethyloxamide by substituting diethylamine for ammonia in the above reaction, led to negative results. This chloride when heated is resolved into diethylcarbamic chloride, $\text{NEt}_2\cdot\text{COCl}$, and carbonic oxide. Hence the former is the product of the action of phosphorus pentachloride on diethyloxamic acid when heat is employed to remove the phosphorus oxychloride. *Diethylcarbamic chloride* is a liquid boiling at $190-195^\circ$, it belongs to the "urea-chlorides" described by Michler (*Ber.*, **8**, 1866; **9**, 396 and 710); when exposed to the air it combines with water to form carbonic anhydride and diethylamine hydrochloride, thus: $\text{NEt}_2\cdot\text{COCl} + \text{H}_2\text{O} = \text{CO}_2 + \text{NEt}_2\text{H}_2\text{Cl}$. Further, diethylamine converts it into tetrethylurea $\text{CO}(\text{NEt}_2)_2$ (Michler, *Ber.*, **8**, 1665).

Phosphorus pentachloride acts on *diethylformamide*, and after removal of phosphorus oxychloride by distillation under reduced pressure, the residue consists of the hydrochloride of a base having the composition $\text{C}_{10}\text{H}_{19}\text{ClN}_2$, as deduced from that of its platinumchloride $(\text{C}_{10}\text{H}_{19}\text{ClN}_2\cdot\text{HCl})_2\text{PtCl}_4$. The free base is a transparent liquid, which is decomposed by heat, with the formation of a derivative of pyrroline, shown by the production from it of pyrrol red. The formation of this base and its relation to pyrroline is expressed by the following equation:—



P. P. B.

Action of Ozone, Nascent Oxygen, and Hydrogen Peroxide on Benzene. By A. R. LEEDS (*Ber.*, **14**, 975—977).—Benzene is oxidised by ozone with formation of carbonic, oxalic, formic, and acetic acids: the explosive ozobenzene described by Houzeau and Renard (*Compt. rend.*, **76**, 572) was not obtained. When benzene is exposed to air which is in contact with moist phosphorus, phenyl and oxalic acid are produced, if the reaction takes place in direct sunlight; but in diffused light only oxalic acid is obtained. Hoppe-Seyler (*Ber.*, **12**, 1551, this Journal, 1880, Abstr., 3), has shown that phenol is produced when the alloy of hydrogen and palladium is shaken with air, water, and benzene. Benzene is also converted into phenol by boiling with a dilute solution of hydrogen peroxide. W. C. W.

Researches on Isomerism: Benzene and Dipropargyl. By BERTHELOT and OGIER (*Compt. rend.*, **91**, 781—787).—L. Henry, of Louvain, the discoverer of dipropargyl, having placed a quantity of this substance at the disposal of the authors, they have determined its heat of combustion and formation, and compared them with those of its isomeride, benzene. Dipropargyl, C_6H_6 , boils at 85° ; benzene at 81° . Its density is distinctly less than that of benzene, 0.82 instead

of 0.89; it is also much less stable, is very easily polymerised, and forms an addition-product with 8 atoms of bromine.

The heat of combustion was measured (*Ann. Chim. Phys.* [5], 13, 15), by placing a known quantity of the substance on cotton, vaporising it in a current of air, and exploding the mixture in a suitable vessel. The combustion was not complete, although no carbon was deposited, but this was allowed for in the calculation. In this way 776 units (kil.-deg.) were obtained for 78 grams (1 mol.) of liquid benzene. Another determination in the calorimetric bomb gave + 783.2 units.

C_6 (diamond) + H_6 = C_6H_6 gas, absorbs - 12.2 units.

C_6 (charcoal) + H_6 = „ „ evolves - 5.8 „

Thus the sum of the work done in the formation of benzene from its elements is small, the heat disengaged being positive or negative, according to the nature of the carbon from which it may be supposed to be derived.

The combustion of the dipropargyl was effected in the calorimetric bomb. As in the case of benzene, the combustion was never complete, no matter how carefully it was executed, and there was always a deposit of carbon. However, a comparison between the initial weight of the hydrocarbon and of the carbonic anhydride produced, enables a valuation to be made of the portion which has been incompletely burnt; this in the best experiments amounted to 1.9 per cent., and in less favourable ones to 6.0 per cent. of the total weight. It was further necessary to reckon the unburnt carbon as corresponding with a portion of the hydrocarbon, of which the hydrogen alone was burnt, whilst the carbon was precipitated.

Ten combustions of dipropargyl gave as a mean + 853.6 units, on supposition that the portion incompletely burned furnished elementary carbon and water, or + 842.8 units if it be reckoned as carbonic oxide and water. The former figure is considered to be nearer the truth. This heat of combustion exceeds by nearly one-tenth the heat of combustion of benzene, and gives for the heat of formation of dipropargyl—

C_6 (diamond) + H_6 = C_6H_6 gas. - 82.8 units.

C_6 (charcoal) + H_6 = „ „ - 64.8 „

Dipropargyl is therefore formed with a considerable absorption of heat, in a manner similar to acetylene (- 61.1), allylene (- 46.5), and ethylene (- 15.4). Its formation from acetylene would disengage 100.5 units, whilst benzene from the same source would evolve nearly double, namely, 171.1 units; the transformation of dipropargyl into benzene would therefore evolve + 70.6 units.

All experiments with a view of effecting this direct change were without result. Heated in a sealed tube to 225°, dipropargyl first polymerised and then decomposed, with carbonisation. At 300°, it was destroyed, with production of a large quantity of gas, but without formation of benzene. Nitric acid attacked it violently, with formation of resinous looking nitro-bodies, but no nitrobenzene; iodine and sulphuric acid polymerised it in a similar manner.

As a rule, it may be taken as proved that there is a disengagement of heat, that is to say, a loss of energy—

(1.) When several distinct elements combine to form a new substance.

(2.) When several identical molecules unite to form a more condensed substance.

(3.) When a body endowed with a certain capacity of saturation is transformed into an isomeride of the same condensation, whose power of forming addition-products is less, as in the conversion of terpene into cymene; in this case there appears to be effected in the substance a sort of internal saturation, which may be supposed to correspond with or be the representative of the "exchange of atomicities" in the case of elements.

J. W.

Electrolysis of Toluene. By A. RENARD (*Compt. rend.*, **92**, 965—966).—The products obtained by electrolysing toluene are mixed with 2 to 3 times their volume of water, the oil which rises to the surface being separated, washed with soda, and dried. After the excess of toluene has been distilled off, the remaining portion boils at 190° , and yields a crystalline mass with hydrogen sodium sulphite, which, on distilling with a concentrated solution of sodium carbonate, gives benzaldehyde. The author obtains phenose from the aqueous solution which remains after separating the oil.

J. I. W.

Preparation of Metatoluidine. By VIENNE and STEINER (*Bull. Soc. Chim.* [2], **35**, 428—429).—The authors state that they have been unable to obtain metatoluidine by following the directions given by Widman. They have employed the following method: Benzaldehyde is nitrated by treating it with a mixture of nitric and sulphuric acids, the product is poured into water, and allowed to stand. The yellow needles which separate out are freed from the oil with which they are mixed by pressure, and then recrystallised from alcohol. They have the composition $C_6H_4(NO_2).COH$. On treating with phosphorus pentachloride, $C_6H_4(NO_2).CCl_2H$ is obtained; but on reduction with either sodium-amalgam or zinc and hydrochloric acid, only a resinous mass of the composition $C_{14}H_{13}N_2ClO_2$ is obtained.

J. I. W.

Dry Distillation of the Mucates of Aniline and Paratoluidine. By L. LICHTENSTEIN (*Ber.*, **14**, 933—937).—On dry distillation, aniline mucate yields phenylpyrroline, $C_{10}H_9N$, and a compound insoluble in benzene, having the composition $C_{16}H_{14}N_2$. Benzylpyrroline, $C_{11}H_{11}N$, and a substance, $C_{18}H_{18}N_2$, insoluble in benzene, are formed by the distillation of paratoluidine mucate. Identical products were obtained by Altmann from aniline and paratoluidine saccharates. Strong nitric acid acts energetically on each of these bodies, converting them into oxalates.

Benzylpyrroline unites with mercuric chloride, forming a crystalline compound, $2(C_4H_4N.C_7H_7)HgCl_2$, and when heated at 50° with acetic chloride in sealed tubes, it yields a crystalline *tetracetic* derivative, $C_4Ac_4N.C_7H_7$.

When bromine is added to a solution of $C_{18}H_{18}N_2$ in benzene, a black

precipitate is produced: the filtrate is evaporated, and the residue extracted with weak alcohol, which leaves triclinic prisms of the compound $C_{18}H_8Br_{10}N_2$ undissolved. This substance is not attacked by ammonia, but by the action of sodium and ethyl or ethylene bromide 2 bromine-atoms can be replaced by ethyl or ethylene, forming $C_{18}H_8Br_8Et_2N_2$ and $C_{18}H_8Br_8(C_2H_4)_2N_2$ respectively. A crystalline powder, having the composition $C_{15}H_{24}N_2(HBr)_2$, is obtained from the black precipitate previously mentioned, by extracting it with alcohol, evaporating the solution to dryness, and digesting the residue in water.

The author represents the constitution of the compound $C_{18}H_{18}N_2$, by the formula $C_7H_7.N \begin{array}{c} \diagup CH.CH \diagdown \\ | \quad | \\ CH.CH \end{array} N.C_7H_7$, and regards it as a derivative of $HN \begin{array}{c} \diagup CH.CH \diagdown \\ | \quad | \\ CH.CH \end{array} NH$.

W. C. W.

New Synthesis of Organic Bases containing Oxygen. By W. STAEDL and O. SIEPERMANN (*Ber.*, **14**, 983—985).—When bromoacetylbenzene is dissolved in dimethylaniline at 70° , trimethylphenylammonium bromide and a base containing oxygen are produced, $2NPhMe_2 + PhCO.CH_2Br = NMePh.CH_2.COPh + NPhMe_3Br$. A similar reaction occurs when bromoacetylbenzene acts on dimethylmetatoluidine. The properties of this base have been already described (*Ber.*, **13**, 841; this Journal, Abstr., 1880, 639).

On heating the base with methyl or ethyl iodide, the reverse of the preceding reaction takes place, iodacetylbenzene and the iodide of an ammonium base being formed.

W. C. W.

Action of Haloid Compounds of Hydrocarbon Radicals on Phosphide of Sodium, and on the Salts of Tetrabenzylphosphonium. By E. A. LETTS and N. COLLIE (*Proc. Roy. Soc. Edin.*, **11**, 46—50).—The exact method for preparing the chloride of tetrabenzylphosphonium from sodium phosphide and benzyl chloride is not detailed in the present paper, but the chloride, $(C_7H_7)_4PCl$, is dissolved out by boiling water, from which it crystallises in large needles (m. p. 224 — 225°). The platinochloride and acid sulphate have likewise been prepared. The hydroxide, $(C_7H_7)_4P.OH$, which is soluble in water, is formed when a dilute solution of the acid sulphate and baryta are brought together; when, however, the solutions are not sufficiently dilute, the oxide of tribenzylphosphine, $(C_2H_7)_3PO$, which is insoluble in water, is produced.

E. W. P.

Arsenobenzene. By A. MICHAELIS and C. SCHULTE (*Ber.*, **14**, 912—914).—*Arsenobenzene*, $PhAs:AsPh$, is deposited as a crystalline mass on gently warming a moderately concentrated alcoholic solution of phenylarsene oxide, $PhAsO$, to which an excess of phosphorous acid has been added. The crystals are collected on a filter, and washed with absolute alcohol. Arsenobenzene is soluble in benzene, chloroform, carbon bisulphide, and in boiling xylene. It combines directly

with chlorine to form phenylarsene dichloride, PhAsCl_2 . Arsenobenzene melts at 196° , and at a higher temperature splits up, forming metallic arsenic and triphenylarsine.

Phenylarsene iodide, PhAsI_2 , is a red oily liquid, obtained by the action of strong hydriodic acid on phenylarsene oxide. On the addition of phosphorus acid to the hot alcoholic solution of the iodide, yellow needle-shaped crystals of iodarsenobenzene, $(\text{PhAsI})_2$, are deposited. This compound is very unstable; it rapidly deliquesces, even when placed over sulphuric acid in a vacuum.

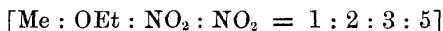
Arseno-naphthalene, $\text{C}_{10}\text{H}_7\text{As}:\text{AsC}_{10}\text{H}_7$, can be prepared by the action of reducing agents on an alcoholic solution of naphthylarsene oxide.
W. C. W.

Preparation of Pure Phenol. By W. ALEXEJEFF (*Bull. Soc. Chim.* [2], 35, 379).—In order to prepare pure phenol, the author adds 5 per cent. of water to the commercial substance, and, after having melted the mixture, allows it to stand. The crystals which gradually form are drained, and after repeating the operation from two to three times, the product is distilled.

Calvert stated that when 4 parts of phenol were agitated with 1 part of water at a temperature below 4° , a hydrate with the composition $2\text{PhHO} + \text{H}_2\text{O}$ (m. p. 16°) was formed. The author has been unable to confirm his observations. He finds, however, that when phenol is allowed to stand for several months with an excess of water, crystals are formed which melt at 37° .
J. I. W.

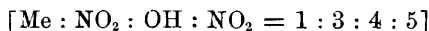
Action of Nitric Acid on some Phenol Ethers. By W. STAEDEL and others (*Ber.*, 14, 898—906).—The ethers employed in this investigation were obtained by the action of methyl iodide, ethyl bromide, and benzyl chloride respectively on the potassium salts of the phenols. For the nitrations, nitric acid of sp. gr. 1.5 was employed, and the action allowed to proceed at 0° .

Orthocresyl ethyl ether, $\text{C}_6\text{H}_4\text{Me.OEt}$, is a colourless liquid (b. p. $180\text{--}181^\circ$ uncorr.; sp. gr. = 0.97123 at 5°), with a pleasant odour; gives on nitration mononitrocresyl ethoxide, $[\text{Me}:\text{OEt}:\text{NO}_2 = 1:2:3 \text{ or } 1:2:5]$ (m. p. 71°), dinitrocresyl ethoxide

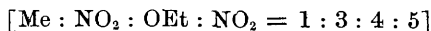


(m. p. 51°), and a little dinitro-orthocresol (m. p. 82°).

Paracresyl ethyl ether on nitration gives dinitroparacresol



(m. p. 84°), ethyl nitrate, and dinitrocresyl ethoxide



(m. p. 75°).

Orthocresyl ethylene ether, $(\text{C}_6\text{H}_4\text{Me})_2\text{C}_2\text{H}_4\text{O}_2$, crystallises in white silky leaflets (m. p. 79°), which are only sparingly soluble in cold, but more easily in hot alcohol.

Benzyl phenyl ether on nitration gives trinitrobenzylphenyl oxide $[\text{C}_6\text{H}_3.\text{NO}_2.\text{NO}_2.\text{OCH}_2.\text{C}_6\text{H}_4.\text{NO}_2 = 1:3:4; 1:4]$ (m. p. 198°), which by the action of alcoholic ammonia at a low temperature

gives paranitrobenzyl alcohol (m. p. 91°), and α -dinitraniline (m. p. 174°).

Benzyl orthocresyl ether, $C_6H_4Me.OCH_2Ph$, is a thick colourless oil (b. p. $285-290^{\circ}$), which gradually becomes yellow, and does not solidify in a freezing mixture. On nitration it gives trinitrobenzyl-cresyl ether [$C_6H_2Me.NO_2.NO_2.OCH_2.C_6H_4.NO_2 = 1 : 3 : 5 : 6 ; 1 : 4$] (m. p. 145°), which by the action of alcoholic ammonia at low temperatures is converted into paranitrobenzyl alcohol and a new dinitro-toluidine (m. p. 208°).

Benzyl paracresyl ether consists of white silky leaflets or transparent six-sided prisms (m. p. 41°), which are insoluble in water, but very easily soluble in alcohol, ether, and benzene. On nitration it gives dinitroparacresol (m. p. 84°), and a compound (m. p. 71°) having the composition and properties of Beilstein and Kuhlberg's (*Annalen*, **147**, 351) dinitrobenzyl alcohol, but which really appears to be paranitrobenzyl nitrate, $C_6H_4(NO_2).CH_2.O.NO_2$, since it gives paranitrobenzoic acid on oxidation.

Benzyl β -naphthyl ether, $C_{10}H_7.OCH_2Ph$, crystallises from alcohol in white brilliant leaflets (m. p. 99°).

Methyl α -naphthyl ether, $C_{10}H_7.OMe$, is a colourless liquid (b. p. 258° , sp. gr. = 1.0974 at 15° ; compare Marchetti, *Gazzetta*, **9**, 544, and Hantzsch, *Ber.*, **13**, 1347), which on nitration gives the trinitro-product $C_{10}H_4(NO_2)_3.OMe$ (m. p. 128°).

Methyl β -naphthyl ether, $C_{10}H_7.OEt$, crystallises from alcohol in large silky plates (m. p. 72°), and on nitration gives a trinitro-product (m. p. 213°). *Ethyl α -naphthyl ether* and *ethyl β -naphthyl ether* on nitration each give a trinitro-product melting at 148° and 186° respectively.

The *dinitroparacresol* (m. p. 84°) referred to above is identical with the compound already known. It forms a methyl ether (m. p. 122°) and an ethyl ether (m. p. 75°), and by the action of alcoholic ammonia at the ordinary temperature gives Beilstein and Kuhlberg's dinitro-toluidine (m. p. 166°), which on oxidation with chromic acid is converted into chrysanic acid (m. p. 258°).

The new *dinitro-orthotoluidine* (m. p. 208°) obtained as above described crystallises in yellow prisms or plates, which have a beautiful blue reflection. It is insoluble in alcohol, and only sparingly soluble in toluene.

Trinitro-naphthylamines.—The two trinitro- α -naphthyl ethers referred to above give trinitro- α -naphthylamine by the action of alcoholic ammonia at a gentle heat. This compound is but sparingly soluble in all solvents, and crystallises from toluene in small yellow leaflets, which darken at 240° , and appear to melt at 264° with decomposition. The two trinitro- β -naphthyl ethers also give a trinitro- β -naphthylamine, which is almost insoluble in all solvents, and crystallises from toluene in yellow needles, which are decomposed at 266° . Both trinitronaphthylamines give a trinitronaphthalene melting at 210° .

Dinitrotoluene, $C_6H_3Me(NO_2)_2$ [$Me : NO_2 : NO_2 = 1 : 3 : 5$], may be obtained either from the dinitroparatoluidine (m. p. 166°), or from the above-described dinitro-orthotoluidine (m. p. 208°), by the diazo-

reaction. It crystallises in needles or prisms (m. p. 91—92°), and from benzene in prisms containing crystallisation benzene, of the composition $C_7H_6(NO_2)_2 + C_6H_6$. On oxidation with chromic acid it gives dinitrobenzoic acid (m. p. 203—204°), the ethyl salt of which crystallises in needles (m. p. 90°). T. C.

Nitro-cresols. By E. NÖLTING and E. SALIS (*Ber.*, **14**, 986—987).—*Dinitroparacresol ethyl ether*, $C_6H_2Me(NO_2)_2.OEt$ [4 : 2 : 6 : 1], formed by the action of ethyl iodide on the silver, lead, or potassium salt of dinitroparacresol, on reduction with tin and hydrochloric acid yields the hydrochloride $EtO.C_6H_2Me(NH_3HCl)_2$. The addition of diazobenzene chloride to a neutral solution of this hydrochloride precipitates chrysoidine.

Dinitro-orthocresol, $[OH : Me : NO_2 : NO_2 = 1 : 2 : 4 : 6]$, prepared by the action of dilute nitric acid on the diazo-compound of orthotoluidine, or by heating the sulphonic acid from orthocresol with dilute nitric acid, melts at 86°.

Trinitrocresol from metacresol melts at 106°, and resembles picric acid in many respects.

Commercial cresol on nitration yields a mixture of dinitro-ortho- and dinitro-para-cresol, which can be separated by the difference in the solubility of their barium salts. No trinitro-derivative is formed.

W. C. W.

Crystallisable Constituents of Corallin. By K. ZULKOWSKY (*Wien. Akad. Ber.*, **82**, 598—605).—The author has continued his work on this subject (*Abstr.*, 1879, 58).

Action of Ammonia on Aurin and Methylaurin.—Aurin heated with alcoholic ammonia at 180° C. gives an orange solution, which becomes deep magenta on concentration. The dry residue dissolves in hydrochloric acid to a brown solution, giving a brassy solid on evaporation. Its aqueous solution is of the same colour as rosaniline salts, of which it gives all the reactions. It dyes with a yellowish magenta tint.

Methylaurin also requires a temperature of 180° for the ammonia reaction, but is more easily converted than aurin. The hydrochloric acid solution of the base is soluble in water and alcohol, giving all the reactions of rosaniline salts. It dyes with a blue or violet magenta tint.

In his previous communication, the author described the formation of oxidised aurin, by direct oxidation of alcoholic solution of aurin. On boiling this oxidised aurin with water, a very complete reduction takes place, aurin being produced in a very pure form; indeed, if filtered boiling, the filtrate will come through after a little time almost colourless.

Aurin, repeatedly and slowly recrystallised, appears to be mixed with the oxidation product, which alters its appearance, and accounts for the supposed existence by the author of an aurin of the formula $C_{18}H_{12}O_3$.

Methylaurin, obtained from rosaniline by the azo-reaction, forms a colourless crystalline hydrocyanide, $C_{20}H_{17}NO_3$, as also does the aurin hydrocyanide. Methylaurin from corallin, however, when treated with potassium cyanide until colourless, and then acidified with

hydrochloric acid, gives a white precipitate, which could not be obtained crystallised.

The methylaurin from corallin behaves towards hydrocyanic acid quite differently from aurin itself or its isomeride from rosaniline.

Both aqueous and alcoholic solutions of aurin rapidly absorb atmospheric oxygen when a large surface of liquid is exposed. The oxidation does not cease at the formation of the compound $C_{19}H_{16}O_6$, its alkaline solution absorbing oxygen more rapidly than aurin itself.

Alkaline solutions of methylaurin also absorb oxygen, but not quite so rapidly as those of aurin. Only one product seems to be formed in both cases.

The author is of opinion that the large amount of tarry products obtained during the recrystallisation of aurin, although previously purified by acid sodium sulphite, is produced by oxidation, only about 60 per cent. of crystallisable substance being obtained from corallin.

W. R. H.

Resorcinol Colouring-matters. By P. WESELSKY and R. BENEDIKT (*Wien. Akad. Ber.* [2], **82**, 1219—1232).—The authors allude at the outset to the incompleteness of former experiments, and the present uncertainty of the constitution of colouring-matters obtained from resorcinol and other phenols.

Diazoresorcinol (of Weselsky).—By the action of nitric acid containing nitrous acid, two mononitroresorcinols are obtained—one new, and the other already known, besides diazoresorcinol. From new analyses it would appear that the formula of diazoresorcinol is $C_{18}H_{20}N_2O_6$, and not $C_{18}H_{12}N_2O_6$, as formerly given by Weselsky. The reaction is as follows:— $3C_6H_5O_2 + N_2O_4 = C_{18}H_{10}N_2O_6 + 4H_2O$.

The nitrate of diazoresorcinol forms golden-green crystals soluble in boiling water.

Ethyl Ether of Diazoresorcinol.—Diazoresorcinol is mixed with alcohol, hydrochloric acid passed in to saturation, and the mixture heated in a sealed tube. The ether, $C_{18}H_{18}Et_2N_2O_6$, forms delicate red-brown interlaced needles (m. p. 202°), which can be sublimed unchanged. It is insoluble in water, soluble in alcohol and ether, and taken up by sulphuric acid, with formation of a blue colour. As this ether is insoluble in potassium hydroxide, it follows that the hydroxylic hydrogen atoms are replaced by ethyl, and also that it is probable that diazo-resorcinol contains two unattacked hydroxyl groups.

Action of Nitrous Acid on the Methyl and Ethyl Ethers of Resorcinol.—The resorcinol ether is saturated with nitric acid containing nitrous acid in a flask cooled with ice, and the crude product of the reaction treated with ether, which throws down "*insoluble colouring-matters*," whilst "*soluble colouring-matters*" remain in the ethereal solution. Among the subsidiary products of the reaction are mononitro-derivatives of the ethers.

Colouring-matters from the Monethyl Ether of Resorcinol Insoluble in Ether.—This body, $C_{21}H_{20}N_2O_6$, forms delicate microscopic claret-red needles (m. p. 230°), insoluble in water and ether, soluble in alcohol; with sulphuric acid it forms an intensely deep purple colour. The colouring-matter soluble in ether forms orange-red needles (m. p. 228°),

of composition $C_{14}H_{11}NO_3$; it gives a blue colour with sulphuric acid.

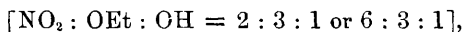
The *monomethyl ether of resorcinol* forms two colouring-matters which resemble the corresponding ethyl derivatives in their external appearance and their reactions.

Nitro-derivatives of resorcinol, one volatile and the other non-volatile, are obtained by the above process; the former crystallises in orange-red prisms (m. p. 88°), which volatilise slowly in the air. With bromine, it is converted in a dibromonitro-resorcinol (m. p. 117°).

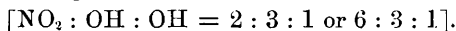
Nitro-derivatives of the Monethyl Ether of Resorcinol.—Two nitro-derivatives are obtained from the monethyl ether of resorcinol; these can be separated by distillation in a current of steam, one being volatile and the other non-volatile. The latter crystallises in compact needles or leaflets (m. p. 131°). It can also be obtained by the oxidation of Aronheim's monethyl ether of nitrosoresorcinol (Abstr., 1879, 465). With bromine, the non-volatile mononitro-derivative forms a dibromo-compound crystallising in needles (m. p. 69°). The volatile ethyl ether of mononitrosoresorcinol forms sulphur-gold needles (m. p. 79°) having a pungent odour; it is sparingly soluble in water, easily soluble in alcohol and ether. The same compound may also be obtained by the action of potassium ethylsulphovinate on the non-volatile mononitrosoresorcinol. With bromine, it forms a monobromo-compound crystallising in golden needles (m. p. 114°).

The *methyl ether of resorcinol* also gives a non-volatile (m. p. 144°) and a volatile (m. p. 95°) nitro-derivative.

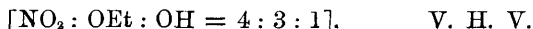
If the volatility of the nitrophenol depends on the close proximity of the hydroxyl and nitro-groups, some insight may be obtained into the corresponding resorcinol derivatives. It is thus probable that the volatile mononitrosoresorcinol derivative has the constitution



and the corresponding mononitrosoresorcinol the constitution



But inasmuch as the ordinary non-volatile nitrosoresorcinol corresponds with the volatile ethyl ether of nitrosoresorcinol, it follows that the former has the constitution $[NO_2 : OH : OH = 6 : 3 : 1]$, and the volatile ethyl ether of mononitrosoresorcinol must then have the groupings in the position $[NO_2 : OH : OH_2 = 3 : 2 : 1]$. As the non-volatile ethyl ether of mononitrosoresorcinol is obtained by the oxidation of the mononitroso-compound, which has the nitroso-group in the paraposition to the hydroxyl group, then it must have the composition



Derivatives of Piperonal. By C. LORENZ (*Ber.*, 14, 785—795).—*Methylenedioxyphenylangelic acid*, $C_{12}H_{12}O_4$, is prepared in a similar manner to methylenecaffeic acid (this Journal, 1881, 48), viz., by heating piperonal sodium acetate and butyric anhydride together for six hours in a vessel with an inverted condenser. The product is treated with water, then extracted with ether, and the ethereal extract treated with sodium carbonate. The free acid is obtained as a white

crystalline precipitate by decomposing the solution of the sodium salt with hydrochloric acid. It is sparingly soluble in water, but largely in alcohol and ether, and crystallises from alcohol in long needles (m. p. 120—160°). Sodium-amalgam acts on an alkaline solution of this acid, forming an oily acid liquid, probably methylenedioxyphenylvaleric acid. The constitution of methylenedioxyphenylangelic acid is represented by the formula $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3.\text{CH} : \text{C}\text{Et}.\text{COOH}$; it is isomeric with the hydropiperic acid obtained by treating the aqueous solution of piperic acid with sodium-amalgam. The fact that piperic acid, when so treated, combines with only two atoms of hydrogen, and further, that on oxidation the chief product is piperonal, shows that its constitution is different from that attributed to it by Fittig (*Annalen*, **152**, 25; **172**, 134; **159**, 129).

The following table contains some of the more important reactions of solutions of the ammonium salts of these acids:—

Reagents.	Piperic acid, $\text{C}_{12}\text{H}_{10}\text{O}_4$; m. p. 216—217°.	Hydropiperic acid, $\text{C}_{12}\text{H}_{12}\text{O}_4$; m. p. 75—76°.	Methylenedioxy- phenylamylic acid, $\text{C}_{12}\text{H}_{12}\text{O}_4$.	Methylenedioxy- phenylvaleric acid; an oil.
Calcium chloride	White floccu- lent precipitate; insoluble in hot water.	No precipitation.	White crystal- line precipitate; soluble in hot water.	White precipi- tate; sparingly soluble in hot water.
Bariumchloride	A white, crystalline precipitate, soluble in hot water.			
Zinc sul- phate	Yellow, sparing- ly soluble salt.	Yellow, sparing- ly soluble salt.	White crystal- line salt; sparing- ly soluble in hot water.	White crystal- line precipitate, sparingly soluble in hot water.
Copper sul- phate	Greenish blue precipitate; slightly soluble in water, solu- ble in NH_3 to a blue solution.	Green, crystal- line precipitate; soluble in NH_3 to a green solu- tion.	Green, curdy precipitate; so- luble in NH_3 to a blue solution.	Bluish-green crystalline pre- cipitate; soluble in NH_3 to a deep blue solution.
Silver ni- trate	—	White precipi- tate, blackening on exposure to light; decom- posed by NH_3 .	White, curdy precipitate; un- stable salt.	White, curdy precipitate; sta- ble salt, soluble in NH_3 .
Lead acetate	—	Yellow crystal- line precipitate; soluble in acetic acid.	White precipi- tate; insoluble in acetic acid.	White precipi- tate; sparingly soluble in acetic acid.
Concentra- ted sulphuric acid and free acid	Brownish-red solution, black- ening when heated.	Cherry-red solu- tion.	Becomes cherry- red on heating.	Cherry-red solu- tion.

Piperonal forms a sparingly soluble compound with sodium hydrogen sulphite, and also exhibits the reaction with rosaniline sulphite, supposed to be characteristic for aldehydes (Schiff, *Annalen*, **150**, 131), viz., the formation of a yellow colour gradually changing to a deep red. This reaction, Tiemann states in a foot-note, is also exhibited by ketones.

When digested with alcoholic ammonia in presence of hydrocyanic acid, piperonal yields a compound having the formula $C_{24}H_{18}N_2O_6$, which crystallises in prisms (m. p. 213°), and is insoluble in alcohol, ether, and glacial acetic acid. It has neither basic nor acid properties. A compound, having the same composition, is obtained by digesting piperonal with alcoholic ammonia at $60-70^\circ$; it is insoluble in water and ether, but soluble in hot alcohol, from which it crystallises in needles (m. p. 172°).

A compound, $C_{14}H_{11}NO_2$, is obtained by heating piperonal and aniline; by crystallisation from light petroleum, it is obtained in colourless needles (m. p. 65°).

Methylenedioxyphenylglycollic acid, $CH_2 : O_2 : C_6H_3.CH(OH).COOH$, is obtained by heating piperonal with hydrocyanic acid at $60-70^\circ$, and saponifying the resulting nitril with hydrochloric acid. It crystallises in granular slightly red crystals (m. p. $152-153^\circ$); it is very unstable, and is decomposed by boiling its aqueous solutions: concentrated sulphuric acid dissolves it, forming a violet solution, which blackens on adding water. Zinc sulphate and silver nitrate produce white precipitates in solutions of the ammonium salt.

Methylenedioxyphenylamidacetic acid,



is obtained by heating the cyanhydrin of piperonal with alcoholic ammonia, and saponifying the resulting amidonitrile. It crystallises in white needles (m. p. 210°), sparingly soluble in water, and insoluble in alcohol and ether; it dissolves in acids and alkalis. In solution of the ammonium salt of this acid, barium and calcium chlorides produce white precipitates, soluble in hot water. The lead salt is obtained as a white amorphous precipitate, soluble in hot water; the zinc salt is a white flocculent precipitate. The copper salt is obtained as a blue precipitate, soluble in ammonia; the ammonium salt gives a green precipitate with ferrous salts, and an orange-coloured precipitate with ferric salts.

P. P. B.

Action of Bromine on Paranitrobenzoic Acid. By W. HALBERSTADT (*Ber.*, **14**, 907—912).—Paranitrobenzoic acid is not readily attacked by bromine, but when it is heated with this reagent in sealed tubes at $270-290^\circ$, the nitro-group is completely eliminated. The chief products of the reaction are parabromobenzoic acid and tetrabromobenzene: parametadibromobenzoic acid and paradibromobenzene are also formed in small quantities.

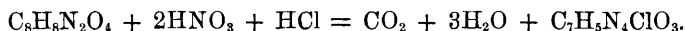
W. C. W.

Dinitrophenylacetic Acid. By S. GABRIEL and R. MEYER (*Ber.*, **14**, 823—833).—Dinitrophenylacetic acid is prepared by dissolving 1 part of phenylacetic acid in 6 parts of fuming nitric acid and adding

to the solution 6 parts of concentrated sulphuric acid; the whole is then poured into water; when crystallised from water, the precipitated dinitro-acid forms fine yellow concentrically grouped needles (m. p. 160°). As shown by Radziszewski (*Ber.*, **2**, 210; **3**, 648), when this acid is heated above its melting point, it is resolved into carbonic anhydride and dinitrotoluene, $[\text{Me} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4]$ (m. p. 71°). Hence dinitrophenylacetic acid is $[\text{CH}_2.\text{COOH} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4]$.

Paramido-orthonitrophenylacetic acid, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2).\text{CH}_2.\text{COOH}$, is obtained by reducing the dinitro-acid with ammonium sulphide. It crystallises in long, broad, reddish-brown needles (m. p. $184\text{--}186^{\circ}$); easily soluble in boiling water and alcohol, sparingly in ether, and insoluble in benzene and carbon bisulphide. Its *ethyl* salt forms long yellow slender needles (m. p. 100°). The *methyl* salt melts at 94° .

The diazo-compounds cannot be prepared from the amidonitro-acid, as decomposition takes place with liberation of carbonic anhydride and the formation of diazo-derivatives of nitroso-methylnitrobenzene. Thus when the amidonitro-acid, dissolved in hydrochloric acid, is treated with amyl nitrite, the *chloride of nitrosomethyl nitro-diazobenzene*, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_3(\text{NO}_2).\text{N}_2\text{Cl}$, is formed, thus:

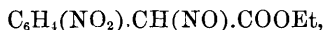


This diazo-compound, when boiled with alcohol, yields a compound having the formula $\text{C}_7\text{H}_5\text{N}_2\text{O}_3$, crystallising from water in slender branching needles (m. p. $96\text{--}97^{\circ}$). It is soluble in fixed alkalis, in benzene, alcohol, and ether, and, to some extent, in carbon bisulphide and light petroleum. That this compound is nitrosomethyl-orthonitrobenzene, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_4.\text{NO}_2$, is shown (1) by its conversion into orthonitrobenzoic acid when heated with hydrochloric acid at $150\text{--}160^{\circ}$, and (2) by its conversion into orthonitrobenzaldehyde, $\text{C}_7\text{H}_5\text{NO}_3$, by oxidation with potassium dichromate and sulphuric acid. The constitution of the oxidation-product was shown by its melting point ($43.5\text{--}44.5^{\circ}$) and by its conversion into orthonitrocinnamic acid by the action of acetic anhydride and sodium acetate.

Nitrosomethyl-orthonitroparabrombenzene, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_4.\text{Br}.\text{NO}_2$, is obtained by treating the diazo-compound, $\text{C}_7\text{H}_5\text{N}_4\text{ClO}_3$, already described, with hydrobromic acid; it crystallises from hot water in groups of slender needles (m. p. $151\text{--}153^{\circ}$) soluble in the ordinary solvents.

Ethyl nitrophenyl-nitrosoacetate, $\text{C}_7\text{H}_5\text{N}_2\text{O}_3.\text{COOEt}$, is obtained by acting on a solution of ethylic amidonitrophenylacetate in hydrochloric acid with an alcoholic solution of ethyl nitrite. After expelling the alcohol, a resin is left from which the ethyl salt may be obtained by extracting with boiling water; it crystallises in long slightly yellow needles (m. p. 163°). It is sparingly soluble in carbon bisulphide and water, but more soluble in alcohol, ether, and benzene. Ammonia does not dissolve it, but it is dissolved by the fixed alkalis to form a yellow solution which gives a yellow precipitate with silver nitrate.

That the constitutional formula for this compound is



is shown by its resolution when heated with hydrochloric acid, into

orthonitrobenzoic acid, carbonic anhydride, ammonia, and ethyl chloride. Like many other nitroso-compounds, *e.g.*, nitroso-oxindol, nitrosomalonyl urea, &c., it combines with alkalis.

Paramido-oxindol, $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CH}_2\\ \text{NH}\end{smallmatrix}\rangle\text{CO}$, is obtained by reducing dinitrophenylacetic acid with tin and hydrochloric acid. It crystallises from hot water in long needles, having a vitreous lustre (m. p. about 200°). It is easily oxidised, yielding resinous products; it is a strong base, and is soluble in water, alcohol, and ether, but only sparingly in benzene and carbon bisulphide.

Paradiazio-nitroso-oxindol chloride, $\text{C}_6\text{H}_3(\text{N}_2\text{Cl})\langle\begin{smallmatrix}\text{CH}(\text{NO})\\ \text{NH}\end{smallmatrix}\rangle\text{CO}$, is obtained by treating the hydrochloric acid solution of paramido-oxindol with amyl nitrite. It crystallises in yellowish-brown needles, and is decomposed but slowly by hot alcohol. P. P. B.

Synthesis of Ketonic Acids. By L. ROSER (*Ber.*, **14**, 940—941).—By the action of amyl chloroxalate on benzene in presence of aluminium chloride, a small quantity of an acid was obtained which dissolved in strong sulphuric acid with a violet coloration. According to the author it is identical with Claisen's benzoylcarboxylic acid. Acids were also obtained by the action of amyl chloroxalate on toluene, naphthalene, and orthonitrotoluene. W. C. W.

Compounds of Phthalic Anhydride with Hydrocarbons of the Benzene Series. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, **92**, 833—837).—Phthalic anhydride reacts readily with the hydrocarbons of the benzene series when equal weights of the anhydride, the hydrocarbon, and aluminium chloride are mixed together and heated for two or three hours on a sand-bath. When the hydrocarbon can be obtained in a state of purity, it is advantageous to employ an excess, about 5 parts to 1 part phthalic anhydride and 1 part aluminium chloride. With benzene and toluene, almost the theoretical yield of the products is obtained, and the excess of the hydrocarbon can be recovered in a state of purity. The product of the reaction is poured gradually into water, and boiled with excess of the latter in order to remove the unaltered aluminium chloride and the greater part of the phthalic anhydride left unattacked. The acid obtained is dissolved in ammonia, precipitated from a boiling solution by means of hydrochloric acid, and purified by crystallisation. Phthalic anhydride and benzene give ortho-benzoyl-benzoic acid, no isomeride of which can exist. The existence of an isomeride of the corresponding toluene compound is theoretically possible, but, as a matter of fact, only one toluyl-benzoic acid has been obtained by this method. It would indeed appear that in all cases of the reaction of phthalic anhydride with a benzene hydrocarbon, only one of the possible isomerides is produced. The authors have not been able to obtain an acid formed by the action of two molecules of phthalic anhydride on the same molecule of benzene. By fusion with potassium hydroxide, benzoyl- and toluyl-benzoic acids are converted into benzoic and paratoluic acids, the latter being free from isomerides. With the deriva-

tives of the higher hydrocarbons the decomposition is more complicated, duroyl-benzoic acid, for example, being converted into durene, benzoic acid, and carbonic anhydride. When an acid homologous with benzoic acid is produced simultaneously with the latter, the reaction affords an excellent means of determining the position of the hydrogen atom replaced by the phthalic group. Investigations have been made in this way with respect to the influence exerted by the position of the methyl groups on the physical properties, especially crystalline form, of compounds of the aromatic series.

Paratoluyyl-orthobenzoic acid, $C_6H_4Me.CO.C_6H_4.COOH$, is obtained by adding 150 grams of aluminium chloride, in small portions at a time, to a mixture of 200 grams toluene and 100 grams phthalic anhydride, and heating the mixture. The following reaction takes place: $-Al_2Cl_6 + C_6H_4(CO)_2O + C_7H_8 = C_7H_7.CO.C_6H_4.COOAl_2Cl_3 + HCl$. This product is decomposed when poured into water, and the new acid may be purified by crystallisation from boiling toluene. It forms hard yellowish crystals which, when dried at 110° melt at 146° , and cannot be distilled without decomposition. The acid and a number of its insoluble salts melt under boiling water. It is only very slightly soluble in hot water, but dissolves readily in alcohol, acetone, and ether. It also dissolves easily in benzene, but the best solvent is boiling toluene, which deposits the greater part of the acid on cooling. The acid is deposited from its solution in a mixture of alcohol and toluene, in the form of small brilliant, transparent triclinic prisms, with curved faces. These crystals contain 1 mol. of water of crystallisation, melt a little above 100° , and gradually give off their water at this temperature, the melting point at the same time rising. The anhydrous acid is obtained in short thick needles by deposition from solution in boiling toluene. Most of its salts form microscopic crystals. The potassium, sodium, and calcium salts are very soluble in water; the barium compound which contains 4 mols. H_2O is only slightly soluble. The cadmium salt forms acicular prisms containing $\frac{1}{2}H_2O$; the copper salt crystallises in long plates containing $4H_2O$, and the silver salt forms slender needles which do not fuse in boiling water. The methyl salt forms short prisms which melt at 53° ; the ethyl salt melts at $68-69^\circ$. Both are soluble in alcohol, and may be distilled with partial decomposition. When the sodium salt is fused with 5 or 6 parts of potassium hydroxide at a little above 300° , it is entirely converted into benzoic and paratoluic acids, indeed this reaction affords the best method of obtaining the latter free from isomerides.

Duroyl-benzoic acid, $C_6HMe_4.CO.C_6H_4.COOH$, is obtained by the preceding method, substituting durene (tetramethylbenzene) for toluene. It melts at above 260° , but the majority of its salts melt when heated with a quantity of water insufficient to dissolve them. It is insoluble in water, but dissolves easily in alcohol, ether, acetone, benzene and toluene, and may be obtained in crystals by deposition from its solution in glacial acetic acid. The ammonium, sodium, and potassium salts are soluble in water; the barium and calcium salts are only slightly soluble and crystallise in needles containing 1 mol. H_2O . The salts of silver, lead, and copper are insoluble, and do not fuse under water.

C. H. B.

Phthalic Anhydride Condensation Products. By S. GABRIEL (*Ber.*, **14**, 919—927).—By the action of acetic anhydride and sodium acetate on acetophenonecarboxylic acid, a derivative, $C_8H_7\ddot{A}cO_3$, is obtained, which crystallises in long colourless needles (m. p. 71°) soluble in alcohol, ether, chloroform, light petroleum, and carbon bisulphide, but is insoluble in alkalis. This body is not an acetic derivative of a hydroxy-acid, but a mixed anhydride of acetic and acetophenonecarboxylic acids, viz., $MeCO.C_6H_4.COO\ddot{A}c$.

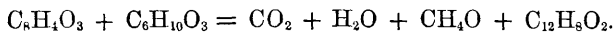
Since acetophenonecarboxylic acid is a derivative of phthalylacetic acid, the formation of the preceding compound is evidence in favour of phthalylacetic acid having the constitution $C_6H_4(CO)_2:CH.COOH$, and not $CO<\overset{O}{\underset{C_6H_4}{\curvearrowright}}>C:CH.COOH$.

On boiling a mixture of phthalic anhydride, phenoxacetic acid and anhydrous sodium acetate, carbonic anhydride is evolved and *phenoxy-methylenephthalyl*, $C_6H_4(CO)_2:CH.OPh$, and a substance melting at 91° are formed. Phenoxy-methylenephthalyl is deposited from an alcoholic solution in needles (m. p. 143°). When boiled with sodium hydroxide it takes up a molecule of water, and on the addition of hydrochloric acid to the alkaline solution, *phenoxyacetophenonecarboxylic acid*, $COOH.C_6H_4.CO.CH_2.OPh$, is deposited in needle-shaped crystals (m. p. 110°).

Cresoxymethylenephthalyl, $C_6H_4(CO)_2:CH.OC_7H_7$, prepared by boiling paracresoxacetic acid with phthalic anhydride and sodium acetate, crystallises in flat needles and plates (m. p. 173°), which are sparingly soluble in hot alcohol.

By the action of phthalic anhydride on ethyl malonate at 130° to 150° (in presence of anhydrous sodium acetate), a mixture of orthotribenzoylbenzene, $C_6(C_6H_4.CO)_3$, and methylenephthalyl is produced. These substances are separated by the solubility of the latter compound in hot glacial acetic acid. Methylenephthalyl forms yellow needles (m. p. 218°).

If ethyl acetoacetate is substituted for the ethyl malonate in the preceding experiment, orthotribenzoylbenzene and a crystalline compound (m. p. 210°) having the composition $C_{12}H_8O_2$, are obtained.



W. C. W.

Mesitylenedisulphonic Acid. By L. BARTH and J. HERZIG (*Wien. Akad. Ber.*, **82** [2], 815—824).—The acid is prepared by warming a solution of 1 part of mesitylene in 10 parts of fuming sulphuric acid, for two or three days, at 30 — 40° , and adding to the solution, at intervals of about 10 hours, 3 to 4 parts of phosphoric anhydride. The product is then poured into water, the sulphurous acid boiled off, and the solution saturated with lead carbonate; the filtrate, after evaporation to dryness, is treated with alcohol to remove any monosulphonate, and the insoluble residue is decomposed with sulphuretted hydrogen. The acid may be further purified by converting it into the potassium salt, crystallising this from 90 per cent. alcohol, and decomposing the lead salt prepared from this with sulphuretted hydrogen. The pure acid crystallises in needles,

which redden slightly in the air, and deliquesce very easily. The potassium salt, $C_6HMe_3(KSO_3)_2 \cdot 2H_2O$, crystallises from alcohol in very beautiful needles, and loses its water of crystallisation at 125° ; the sodium salt forms dull white needles with $1\frac{1}{2}H_2O$, which go off at 100° ; the copper salt, $C_6HMe_3(SO_3)_2Cu$, is deposited from a very concentrated solution, when it is left over sulphuric acid, in whitish-green deliquescent needles, which blacken at 120 – 130° ; the barium salt forms small pointed needles with $3H_2O$, which it loses at 105° ; it decomposes and turns brown at 115° . On fusing the potassium salt with potassium hydroxide, not above 250° , it gives hydroxymesitylenic acid, identical with Fittig's (*Annalen*, **150**, 334) from the monosulphonic acid, the barium salts differ slightly, in the latter case (*loc. cit.*) forming hard crystals with $5H_2O$, in the former soft leaflets with $6H_2O$.

Sodium hydroxide acts at first like potassium hydroxide, but on raising the temperature it completely carbonises the acid. Distillation with potassium cyanide yields chiefly mesitylene, there is also a very small quantity of a nitrogenous body formed crystallising in needles. By fusion with sodium formate, it yields chiefly tarry products with very little acid; on distilling potassium mesitylenedisulphonate alone, it gives a quantitative yield of mesitylene. Bromine acts on the potassium salt, producing dibromomesitylene. From the last two reactions, it would seem that both sulphonic groups are in the benzene-nucleus. As the authors could not prepare a trisulphonic acid, and as Senhofer under similar conditions made benzene and phenoltrisulphonic acids, but with toluene got only a disulphonic acid, it seems almost as if the presence of hydrocarbon side-chains in the benzene nucleus generally renders the introduction of sulphonic groups more difficult.

D. A. L.

Methylketole. By O. R. JACKSON (*Ber.*, **14**, 879–888).—This compound, which appears to be a secondary base, and probably a homologue of indole, was prepared by the process previously described by Baeyer and the author (*Ber.*, **13**, 187).

It is sparingly soluble in hot water, and on cooling crystallises therefrom in needles (m. p. 59°). It is easily soluble in ether and in alcohol, has the odour of indole, although less intense, and imparts a red stain to a piece of pine wood which has been exposed to the action of hydrochloric acid gas. It differs from indole in its action towards nitrous acid, being coloured yellow thereby, and after a time deposits an amorphous yellow powder. It forms a somewhat unstable *platinochloride* $(C_9H_9N.HCl)_2.PtCl_4 + 3H_2O$, which is decomposed into its constituents by cold water. The vapour-density of the free base corresponds with the formula C_9H_9N , and the compound has probably the

following constitution: $NH \begin{array}{c} \diagup C_6H_4 \\ \diagdown CMe \end{array} = CH$.

Acetylmethylketole, $C_9H_9N\bar{A}c$, crystallises in colourless needles (m. p. 195 – 196°), sparingly soluble in water, but easily soluble in alcohol and in benzene. It is soluble in concentrated hydrochloric acid, and forms a platinochloride. It is not decomposed by

boiling sodium hydroxide, but on heating it with concentrated hydrochloric acid, methylketole is re-formed.

Hydromethylketole, $C_9H_{11}N$, obtained by the action of tin and hydrochloric acid on methylketole, is a colourless oil, heavier than water, and having a characteristic pungent odour, similar to that of piperidine. It is a strong base, and forms a crystalline hydrochloride and platinochloride. *Acetylhydromethylketole*, $C_9H_{10}N\dot{A}c$, is formed by the action of acetic anhydride on hydromethylketole, and crystallises in snow-white needles (m. p. $55-56^\circ$), which are easily soluble in all the ordinary solvents, except water. It is a feeble base, dissolving only in concentrated hydrochloric acid, and forming a solution from which the platinochloride may be obtained. *Nitrosohydromethylketole*, $C_9H_{10}N\cdot NO$, is obtained by the action of sodium nitrite on the hydrochloric acid solution of the base, as an oil which subsequently becomes crystalline. It forms compact yellow crystals (m. p. $54-55^\circ$), which are easily soluble in alcohol, in ether, and in hot light petroleum. It dissolves in strong sulphuric acid with a violet colour, and gives Liebermann's reaction with phenol and sulphuric acid.

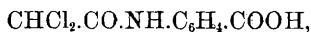
It dissolves in concentrated hydrochloric acid with a red colour; and the solution on reduction with tin gives hydromethylketole. These reactions show that the latter is a secondary base, and that the

nitroso-compound must have the constitution $NO\cdot N \begin{matrix} \swarrow C_6H_4 \\ \searrow CHMe \end{matrix} CH_2$.

Methylketole on oxidation with potassium permanganate gives *acetylorthoamidobenzoic acid*, crystallising in plates or needles (m. p. $179-180$), which are moderately soluble in hot, only sparingly in cold water, but easily in alcohol, ether, and glacial acetic acid. It is only slightly basic, and does not give a platinochloride. It is decomposed into anthranilic acid (m. p. $143-144^\circ$), and acetic acid on boiling with concentrated hydrochloric acid. It is therefore identical with the acid obtained by Bedson and King (this Journal, Trans., 1880, 752) by the oxidation of orthoacetoluide.

Monobromacetylorthoamidobenzoic acid, $C_9H_5BrNO_3$, obtained by the action of bromine on the preceding compound, crystallises in white needles (m. p. $214-215^\circ$).

By the action of phosphorus pentachloride acetylorthoamidobenzoic acid gives an acid having the constitution—



crystallising in yellow needles (m. p. 173°). It is devoid of basic properties, and on boiling with hydrochloric acid, gives anthranilic acid, but no acetic acid.

By slightly varying the mode of treatment after the action of the phosphorus pentachloride on the acetylorthoamidoacetic acid, the compound $C_9H_5ClNO_3$ is obtained, as a yellow crystalline body, which on heating cakes together at $135-140^\circ$, and is decomposed at 200° without melting completely. It is possibly a mixture of the original acid with the dichlorinated product.

T. C.

β -Derivatives of Naphthalene. By P. JACOBSEN (*Ber.*, **14**, 803—807).— β -Naphthylamine nitrate, $C_{10}H_7.NH_2.HNO_3$, crystallises in colourless leaflets, soluble in cold water.

β -Iodonaphthalene, $C_{10}H_7I$, is obtained by decomposing β -diazonaphthalene sulphate with hydriodic acid; it is volatile in steam, and crystallises in colourless leaflets, soluble in ether, alcohol, and glacial acetic acid (m. p. 545°). Its ethereal solution is unacted on by sodium and iodides of alcohol-radicles, and also by zinc ethide. Sodium and ethyl iodide, when heated with the benzene or toluene solution, yield naphthalene, and with the solution in higher boiling liquids, small quantities of ethylnaphthalene are formed.

Nitro- β -acetonaphthalide, $C_{10}H_6(NO_2).NHAc$, is obtained by adding nitric acid (sp. gr. 1.5°) to a solution of acetonaphthalide in glacial acetic acid. It crystallises from alcohol in beautiful yellow needles (m. p. 123.5°); it is soluble in hot water, in alcohol, and glacial acetic acid.

Nitro- β -naphthol, $C_{10}H_6(NO_2).OH$, is obtained, like the corresponding α -derivative (Andreoni and Biedermann, *Ber.*, **6**, 342), by boiling the nitro-acetonaphthalide with potassium hydroxide. It crystallises from alcohol in short needles, soluble in hot water (m. p. 103°).

Amido- β -naphthol, $C_{10}H_6(NH_2).OH$, is obtained by reducing the nitro-derivative with tin and hydrochloric acid. The hydrochloride of amido- β -naphthol, $C_{10}H_6(OH).NH_2.HCl$, crystallises in white needles. The picrate forms yellow needles, and ferric chloride and bleaching powder give brown precipitates, with solutions of the hydrochloride. This amido- β -naphthol was oxidised in order to convert it into β -naphthoquinone, which, according to Stenhouse and Groves (*Annalen*, **189**, 153), melts at 96° , whereas the author obtained a product which did not melt at 140° . This difference is perhaps to be explained by the fact that the nitro- β -naphthol of these authors melts at 96° , whereas that of the author melts at 103° .
P. P. B.

Synthesis of Homologues of Anthracene. By C. LIEBERMANN and G. TOBIAS (*Ber.*, **14**, 795—803).—In the preparation of amylnanthranol by the method already described (this vol., 608), the formation of an oil is observed. In some cases, its alcoholic solution, when treated with hydrochloric acid, yields amylnanthracene, $C_{14}H_9.C_5H_{11}$. This is easily soluble in light petroleum, ether, benzene, and hot alcohol, and crystallises from the latter in long needles (m. p. 59°), having a pale sea-green colour. Its solutions exhibit a blue fluorescence. It dissolves in concentrated sulphuric acid, forming a green solution, which becomes red when heated. Its picric acid compound crystallises in brownish-red crystals (m. p. 115°). The hydrocarbon is oxidised by chromic acid to amyloxanthrol

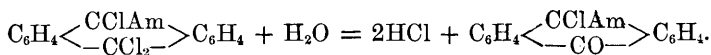
(*loc. cit.*): hence its constitution is $C_6H_4 \begin{array}{c} \diagup \text{C} \text{Am} \diagdown \\ | \\ \text{CH} \end{array} C_6H_4$.

Amylmonobromanthracene, $C_6H_4 \begin{array}{c} \diagup \text{C} \text{Am} \diagdown \\ | \\ \text{CBr} \end{array} C_6H_4$, is obtained by adding

bromine to a solution of amylnanthracene in carbon bisulphide; it crystallises from alcohol in yellow needles (m. p. 76°); its solutions

exhibit fluorescence. The picric acid compound crystallises in orange-yellow needles (m. p. 110°).

Amylmonochloranthracene, $C_{14}H_9Cl.C_5H_{11}$, is obtained by the action of chlorine on a solution of the hydrocarbon in chloroform; it crystallises from alcohol in yellow needles (m. p. 70—71°), and forms a compound with picric acid. If the hydrocarbon is dissolved in carbon bisulphide, some sulphur dichloride is formed, together with amyl-oxanthrol chloride (*ibid.*, **14**, 459). The formation of this latter is explained by the action of the moisture of the air upon amylchloranthracene dichloride, thus:—



The production of amylanthracene is explained by the formation of *amylhydroanthranol*, when anthraquinone is treated with zinc-dust (free from oxide), sodium hydroxide, and amyl bromide. Amylhydroanthranol is precipitated from its alcoholic solution by water as an oil, which solidifies on cooling, and may then be crystallised from alcohol. Its constitutional formula is $C_6H_4 \left\langle \begin{array}{c} \text{CAm(OH)} \\ -\text{CH}_2- \end{array} \right\rangle C_6H_4$; it is resolved into water and amylanthracene, when its solution is treated with hydrochloric acid or sulphuric acid, or by boiling with solution of picric acid. It loses water when dried over sulphuric acid or in a vacuum.

Isobutylhydroanthranol is prepared like the above by substituting isobutyl bromide for amyl bromide. It yields *isobutylanthracene*, $C_{14}H_9.C_4H_9$, crystallising in fluorescent needles (m. p. 57°), and forming a brownish-red compound with picric acid.

The above substituted hydroanthranols may also be obtained in a similar manner to hydroanthranol (Perger, *J. pr. Chem.*, **23**, 137), viz., by heating the substituted oxanthranol with zinc-dust and ammonia. In this manner, ethylhydroanthranol was prepared, and by boiling its alcoholic solution with picric acid, the picric acid compound of ethylanthracene was obtained, which, when decomposed with ammonia, yields the hydrocarbon *ethylanthracene*, $C_{14}H_9Et$. This is more easily soluble in alcohol than the butyl compound, and crystallises in large leaflets united to globular masses (m. p. 60—61°). It is isomeric with Fittig's atranol and Goldschmidt and Hepp's dimethyltolane.

P. P. B.

Anthraquinone Derivatives. By A. CLAUS and A. HERTEL (*Ber.*, **12**, 977—982).—Dibromanthracene dissolves in cold nitric acid (sp. gr. 1.49), forming *mononitro-anthraquinone* (m. p. 230°), which is precipitated on the addition of water. This process gives a better yield of mononitro-anthraquinone than the method described by Böttger and Petersen (*Annalen*, **166**, 148). If the solution of dibromanthracene in nitric acid is heated, the α -dinitroanthraquinone of Böttger and Petersen (*Annalen*, **160**, 147) is produced. When an alcoholic solution of mononitro-anthraquinone is treated with sodium amalgam, the nitroquinone is first formed, but by using an excess of the amalgam, *amidoanthraquinone* is obtained. After removing a portion of the

alcohol by evaporation, water is added to throw down the amido-anthraquinone. This substance crystallises in needles of a beautiful red colour (m. p. 254°). It is identical with the amido-anthraquinone of Böttger and Petersen, but differs from that described by Perger (*Ber.*, **12**, 1566, this Journal, 1880, Abstr., 49).

Strong nitric acid (sp. gr. 1.49) acts energetically on tribromanthracene, forming monobromanthraquinone and other products, which have not yet been isolated.

Mononitromonobromanthraquinone is prepared by boiling tetrabromanthracene in fuming nitric acid and pouring the solution into water. By recrystallising the precipitate from hot acetic acid, white needles (m. p. 261°) are obtained, which are sparingly soluble in ether, alcohol, and chloroform. On reduction with sodium amalgam, the alcoholic solution of nitrobromanthraquinone yields the same amido-anthraquinone as that obtained from nitroanthraquinone.

Dibromanthracene tetrabromide dissolves slowly in hot fuming nitric acid. The addition of water to the acid solution precipitates *dinitrotetrabromanthraquinone* and a small quantity of a white powder, sparingly soluble in water.

Dinitrotetrabromanthraquinone (m. p. 105°) is soluble in alcohol, ether, benzene, and glacial acetic acid. On reduction with sodium amalgam, α -diamidoanthraquinone, described by Böttger and Petersen (*Annalen*, **160**, 149), is formed. W. C. W.

Essence of Linaloes. By H. MORIN (*Compt. rend.*, **92**, 998—1000).—Essence of linaloes, or *Licari kanali*, the white cedar of Cayenne, is a slightly coloured limpid liquid, of agreeable aromatic odour, like rose and lemon. It burns with a smoky flame. In order to obtain it pure, it is dried over calcium chloride and then distilled. It boils at 198° at 755 mm. Its sp. gr. at 15° is 0.868. Its lævoro-rotatory power at 15° is -19° . It is soluble in alcohol, ether, and glycerol. It is violently acted on by bromine, iodine, and nitric acid. It absorbs hydrochloric acid gas in the cold, forming a thick liquid, with a camphor-like odour. The composition of the essence is identical with that of Borneo-camphor, $C_{20}H_{18}O_2$. When treated with fused zinc chloride, it loses water and yields, like the essences of eucjeput and *Osmitopsis astericoides*, a hydrocarbon, $C_{20}H_{16}$, with an odour resembling turpentine. J. I. W.

Products of the Distillation of Colophony. By A. RENARD (*Compt. rend.*, **92**, 887—890).—In addition to the hydrocarbon *heptene*, described in a previous paper (this Journal, 1880, Abstr., 893), the author has obtained two new products, one of which boils at about 154° , and apparently consists of a mixture of terebenthene, with a hydrocarbon, $C_{10}H_{18}$; the other boils at 170 — 173° . This latter product consists mainly of a hydrocarbon, $C_{10}H_{16}$, which is lævorotatory, and absorbs oxygen more rapidly than terebenthene. When left in presence of water or a mixture of alcohol and nitric acid for several months, it forms no crystalline hydrate. It is attacked violently by fuming nitric acid, but the ordinary acid only reacts at about 80° , forming nitro-toluic and oxalic acids, and a soluble syrupy acid which has not been

studied. When hydrochloric acid is passed into an ethereal solution of the hydrocarbon, the hydrochloride, $C_{10}H_{16}.2HCl$, is formed. It crystallises from alcohol in large nacreous plates, which melt at 49° . The prolonged action of bromine with exposure to light yields a tetrabromo-derivative, $C_{10}H_{12}Br_4$, a very thick, orange-coloured liquid. If the action be allowed to go on for one day only in the dark, crystals are obtained of the composition $C_{10}H_{12}Br_4$, apparently isomeric with the preceding compound. When an ethereal solution of the hydrocarbon is added to an ethereal solution of bromine until the latter is decolorised, the compound $C_{10}H_{16}Br_4$ is obtained in colourless crystals, which melt at 120° . Both bromine and hydrochloric acid combine only with a portion of the hydrocarbon. Treated with its own volume of sulphuric acid, the hydrocarbon is converted into a cymene-sulphonic acid, the barium salt of which has the composition $(C_{10}H_{13}SO_3)_2Ba + H_2O$. By long contact with one-twentieth its volume of sulphuric acid, the hydrocarbon is converted into a polymeride, $C_{20}H_{32}$, which boils at $305\text{--}310^\circ$, and is but little altered by exposure to air, cymene, and a hydrocarbon, $C_{10}H_{16}$ (b. p. $171\text{--}173^\circ$), which absorbs oxygen much less rapidly than terebenthene. Its sp. gr. at $11^\circ = 0.8611$. With nitric acid, bromine, and sulphuric acid, it forms the same compounds as the original hydrocarbon, but the action in each case takes place much less readily. C. H. B.

Hesperidin and its Derivatives. By F. TIEMANN and W. WILL (*Ber.*, **14**, 946—974).—Hesperidin is contained in the fruit, leaves and stalks of several members of the *Aurantaceæ*. It is best obtained from dried unripe oranges by Hilger's process (*Ber.*, **9**, 26—31; this Journal, 1876 [i], 709). Instead of purifying the crude product by recrystallisation from acetic acid, it is better to dissolve it in a cold dilute solution of potassium hydroxide, to which a small quantity of alcohol has been added, and then precipitate slowly with carbonic anhydride. The pure glucoside, $C_{22}H_{36}O_{12}$, is a white crystalline hygroscopic mass, devoid of taste and smell. It is insoluble in ether, and only sparingly soluble in alcohol and in water. It melts at 251° with decomposition. On adding hydrochloric acid to the orange-coloured solution produced by treating hesperidin with sodium amalgam, a precipitate is thrown down which dissolves in alcohol, forming a reddish-violet liquid. It has been previously pointed out by E. Hoffmann (*Ber.*, **9**, 685—690; this Journal, 1876 [ii], 420) that hesperidin is resolved into glucose and *hesperetin*, $C_{16}H_{14}O_6$, by dilute acids. This reaction is best accomplished by heating the glucoside at 115° with six parts of a mixture of equal volumes of alcohol and water, containing 2 per cent. of sulphuric acid. The hesperetin, precipitated from the mixture by the addition of water, is dissolved in alcohol, and the colouring matter removed by precipitation with lead acetate. The filtrate is acidified with acetic acid and mixed with warm water, which causes the pure hesperetin to be deposited in white glistening plates. The crystals dissolve freely in alcohol, and sparingly in ether, chloroform, and benzene. Hesperetin melts at 226° with decomposition. On treatment with sodium amalgam, the same product is obtained as in the case of hesperidin. Hoffmann (*loc. cit.*) observed that hesperetin

is decomposed by potassium hydroxide at 100° , forming *hesperitic acid* and phloroglucin. This acid melts at 228° , and is identical with *isofेरulic acid*, $C_6H_3(CH:CH.COOH)(OH)(OMe)$ [1 : 3 : 4], which Tiemann and Nagai (*Ber.*, **11**, 654; this Journal, 1878, Abstr., 580) obtained from caffeic acid. On fusion with potassium hydroxide, protocathechuic acid is formed, and when heated at 160° with dilute hydrochloric acid, an alcoholic chloride and caffeic acid are produced. When a solution of hesperitic acid in methyl alcohol is boiled with methyl iodide and potassium hydroxide, the methyl salt of methylhesperitic acid is obtained, crystallising in prisms (m. p. 64°). Methylhesperitic acid, $C_{11}H_{12}O_4$, prepared by the saponification of the methyl salt, crystallises in needles (m. p. 180°), which are soluble in alcohol and ether. By oxidising a dilute alkaline solution of methylhesperitic acid with potassium permanganate, *veratric acid*, $C_6H_3(COOH)(OMe)(OMe)$ [1 : 3 : 4], is obtained.

Acetylhesperitic acid, $C_6H_3(C_3H_3O)(O\bar{A}c)(OMe)$ [1 : 3 : 4], a crystalline compound formed by boiling hesperitic acid with acetic anhydride, is converted into *isovanillic acid* by oxidation with potassium permanganate; at the same time a small quantity of isovanillin is produced.

Methyl hesperitate, $C_6H_3(C_2H_2.COOMe)(OH).OMe$, crystallises in colourless needles (m. p. 79°), soluble in alcohol and ether.

Hesperetol, $C_6H_3(CH:CH_2)(OH)(OMe)$ [1 : 3 : 4], is best prepared by the dry distillation of calcium hesperitate. It melts at 57° , and is soluble in alcohol, ether, and in strong sulphuric acid, forming in the latter case a carmine-coloured solution. It is dissolved by alkalis and reprecipitated by acids.

The authors represent the constitution of hesperetin by the formula $(MeO)(OH)C_6H_3-CH^1:CH^2.CO.O-(C_6H_3)(OH)(OH)$.

The *Aurantiacæ* contain, in addition to hesperidin, a more soluble glucoside, which appears to have almost the same percentage composition as hesperidin.

W. C. W.

Constituents of the Seeds of *Cocculus Indicus*. By E. SCHMIDT and E. LÖWENHARDT (*Ber.*, **14**, 817—822).—The authors agree with Paternò and Oglialoro (this vol., 440) in regarding picrotoxin as a compound of picrotoxinin and picrotin. In support of their statement, the following facts are cited:—(1.) Picrotoxin melts constantly at $199-200^{\circ}$. (2.) It does not lose weight when heated at 100° , whereas picrotoxinin crystallises with 1 mol. H_2O , which it loses at 100° . (3.) Picrotoxin, when heated with a large quantity of benzene in the cold, expands considerably, a phenomenon not exhibited by either picrotoxinin or picrotin. Moreover picrotoxin so treated undergoes no change in composition, which would scarcely be the case if it were a mixture of two compounds so differently soluble in benzene as picrotoxinin and picrotin (100 parts of benzene dissolve 0.346—0.359 of picrotoxinin, and 0.0199—0.0216 of picrotin at $21-22^{\circ}$).

Picrotoxinin crystallises from water in rhombic tables having the composition $C_{15}H_{16}O_6 + H_2O$ (m. p. $200-201^{\circ}$). Its monobrom-

derivative, $C_{15}H_{15}BrO_6$ (m. p. 245°), is obtained by the action of bromine on its ethereal solution or on the ethereal solution of picrotoxin, which is first decomposed into picrotoxinin and picrotin. The authors regard $C_{21}H_{24}O_{10}$ as the formula for picrotin (m. p. $240-245^\circ$), and picrotoxin is said to have the formula $C_{36}H_{40}O_{16}$: hence its decomposition into picrotin and picrotoxinin is expressed as follows:—



Picrotoxinin dissolves in concentrated sulphuric acid with an orange-red coloration; picrotin gives a pale yellow, becoming orange when heated. Picrotoxin exhibits Langley's reaction with nitric acid, whereas picrotin gives a yellow coloration only.

Acetic chloride acts on picrotoxin, forming an acetyl derivative; picrotoxinin and picrotin are also produced, and the former is converted into a polymeride (m. p. 225°). Hydrochloric acid gas in some cases acts on picrotoxin suspended in ether, and it is then resolved into picrotin and picrotoxinin, the latter being converted into the polymeride, "picrotoxide" (Abstracts, 1879, 729).

By fusing picrotoxin with potassium hydroxide, or heating it with an alcoholic potash solution, resinous bodies are obtained, and some oxalic, formic, and acetic acids. The distillation of picrotoxin with soda-lime and zinc-dust yielded no definite results.

Beside picrotoxin, the authors have obtained from the seeds of *C. indicus* a compound crystallising in white needles, sparingly soluble in hot water, insoluble in cold water, alcohol, and ether. Analysis indicates the formula $C_{19}H_{26}O_{10}$, and the authors designate the compound as *cocculin*. Its taste is not bitter, neither does it exhibit Langley's nitric acid reaction; it dissolves in concentrated sulphuric acid, with a slightly yellow colour. The authors regard it as possibly identical with Barth and Kretschy's *anamirtin* (this vol., 286). P. P. B.

Bromine-derivatives of Quinoline. By W. LA COSTE (*Ber.*, 14, 915—918).—A solution of quinoline hydrochloride combines with bromine to form unstable addition compounds. When a concentrated solution of quinoline hydrochloride is heated with bromine at 180° in sealed tubes, a mixture of mono-, di-, and tri-bromoquinoline is produced. The contents of the tubes are treated with warm dilute hydrochloric acid, which leaves the greater portion of the tribromoquinoline undissolved; the remainder is precipitated by the addition of water. After extracting the dibromoquinoline from the filtrate by ether, sodium hydroxide is added to the aqueous solution, and a mixture of quinoline and monobromoquinoline is precipitated. The quinoline is removed by means of a hot solution of tartaric acid, and the residue is dissolved in dilute hydrochloric acid. The solution, after treatment with animal charcoal and evaporation, deposits monoclinic prisms of monobrombquinoline hydrochloride, $C_9H_6BrN.HCl$. This salt is decomposed by sodium hydroxide, yielding monobromoquinoline in the form of an oily liquid (b. p. 270°). The free base combines with methyl iodide to form a compound crystallising in golden needles or plates. The *platinochloride*, $(C_9H_6BrN.HCl)_2.PtCl_4$, crystallises in needles of an orange colour.

Dibromoquinoline, $C_9H_5Br_2N$, is deposited from alcoholic or acid solutions in needles (m. p. 125°). On the addition of the alcoholic solution to platinum chloride dissolved in alcohol, the compound $(C_9H_5Br_2N.HCl)_2.PtCl_4$ is precipitated. W. C. W.

Tetrahydromethyl-quinoline. By O. R. JACKSON (*Ber.*, **14**, 889—891).—This compound, which is a homologue of methyl-ketole (p. 734),

and has the constitution $HN \begin{array}{c} \diagup C_6H_4 \cdot CH_2 \\ | \\ CHMe \cdot CH_2 \end{array}$, was obtained, as previously

described by Bayer and the author (*Ber.*, **13**, 115), by the nitration and subsequent reduction of methylphenethyl ketone. It is an oil (b. p. 243 — 246°) with a somewhat sweet taste. The hydrochloride is but sparingly soluble in water, and crystallises therefrom in needles. It is easily soluble in alcohol, but insoluble in ether, and forms a platino-chloride.

The methylphenethyl ketone employed in the above reaction was obtained more easily than by Ehrlich's process (*Annalen*, **187**, 11), by heating together a mixture of the calcium salts of hydrocinnamic and acetic acids. It boils at 233 — 234° (bar. 725 mm.). T. C.

Cinchonic Acid and Quinoline-derivatives. By H. WIEDEL and A. COBENZL (*Wien. Akad. Ber.*, **82** [ii], 986—1010).— α -Cinchoninesulphonic acid, $C_{10}H_6NO_2.HSO_3 + H_2O$, is made by heating for six hours at 170 — 180° a mixture of 1 part cinchonine, 2 parts phosphoric anhydride, and 2 parts sulphuric acid. The product when cold is poured into water, and the acid separates out. When pure it forms colourless transparent glistening crystals* (triclinc), only soluble in water when boiled with it for some time, insoluble in all ordinary solvents. At 100° it loses its 1 mol. of water; at a tolerably high temperature it remains undecomposed, and neither sublimes nor melts; at a very high temperature it burns, and leaves a dense coke. It is strongly acid, with a lasting and intensely bitter taste. The *potassium salt* forms slender silky needles, only slightly soluble in water; the *ammonium salt*, $C_{10}H_5NSO_5(NH_4)_2 + 2H_2O$, large colourless shining plates* (monoclinic), very soluble in water, slightly in alcohol, losing their water of crystallisation at 100° . The *calcium salt*, $C_{10}H_5NSO_5.Ca + 2\frac{1}{2}H_2O$, precipitated from the ammonium salt, small, feebly brilliant needles in drusy aggregations, very slightly soluble in water; they lose their water at 240° . The *barium salt*, sparingly soluble, hard, white, glistening crystalline grains* (triclinc), with $3H_2O$, of which 2 mols. H_2O are driven off at 150° , and the remaining H_2O at 260 — 280° . The *neutral copper salt*, $C_{10}H_5NSO_5.Cu + H_2O$, from the ammonium salt by copper acetate, separates on standing as a hard crust of sea-green microscopic crystals, almost insoluble in water, losing the 1 mol. H_2O at 150 — 160° : from the acid, a light green heavy crystalline precipitate is formed, apparently a double compound of the above normal salt with copper acetate. The *lead salt*, obtained by adding basic lead acetate to a dilute solution of the acid, and leaving the liquid at rest for some

* There are measurements by Brezina of the crystals marked thus *.

days, crystallises out in globular masses of long fine silky needles, with 1 mol. H_2O , which it loses at 200° , sparingly soluble in water.

By carefully fusing the acid with potassium hydroxide, α -hydroxycinchonic acid, $\text{C}_{10}\text{H}_6\text{NO}_2\cdot\text{OH} + \text{H}_2\text{O}$, is formed, which, after purification by means of its barium salt, crystallises in pale yellow microscopic glittering needles, very sparingly soluble in water, &c., more soluble in alcohol, fusel oil, and glacial acetic acid. On heating, it partly sublimates and partly fuses (m. p. $254\text{--}256^\circ$, uncorr.).

In the aqueous solution, silver nitrate gives a yellow crystalline precipitate; lead acetate, a precipitate soluble in excess of the reagent; basic lead acetate, no precipitate; ferric chloride produces a green coloration, which turns blackish-green on adding sodium carbonate; and copper acetate precipitates yellowish-green flocks.

The acid combines with both acids and bases; the former compounds are very easily decomposable. It loses its water of crystallisation at 105° . The neutral salts decompose easily, turn dark in the air, crystallise badly, and are coloured greenish even by the smallest trace of iron. The neutral barium salt, $(\text{C}_{10}\text{H}_6\text{NO}_3)_2\text{Ba}$, forms irregular aggregations of very small pale yellow crystals, soluble in water. On adding barium hydrate to this solution, the basic barium salt, $\text{C}_{10}\text{H}_5\text{NO}_3\text{Ba} + \text{H}_2\text{O}$, is precipitated in very pale yellow pointed needles, losing the water of crystallisation at 130° . The silver salt, $\text{C}_{10}\text{H}_6\text{NO}_3\text{Ag}\cdot\text{C}_{10}\text{H}_7\text{NO}_3 + \text{H}_2\text{O}$, is precipitated from the acid in lemon-yellow flocks, which quickly change to microscopic needles. They are almost insoluble, and are not affected by light. The water of crystallisation goes off at 105° . On adding silver nitrate to the barium salt, the salt, $\text{C}_{10}\text{H}_6\text{NO}_3\text{Ag}$, is obtained in small yellowish-white needles, which turn brown on standing. The hydrochloride, $\text{C}_{10}\text{H}_7\text{NO}_3\cdot\text{HCl} + \text{H}_2\text{O}$, orange-yellow glittering needles* (monoclinic), on heating loses part of its hydrochloric acid. The platinochloride, $(\text{C}_{10}\text{H}_7\text{NO}_3\cdot\text{HCl})_2\cdot\text{PtCl}_4$, forms pale yellow needles, somewhat like asbestos, easily decomposed both by water and hydrochloric acid. Its water of crystallisation goes off very easily.

By dry distillation, α -hydroxycinchonic acid yields hydroxyquinoline, called by the authors α -quinophenol, which, after repeated distillations crystallises in beautiful long glassy needles, only slightly soluble in water, easily in alcohol, &c. When cold, it smells like saffron, at higher temperatures like phenol; its taste is bitter, and afterwards burning (m. p. $69\text{--}70^\circ$, uncorr.). Vapour-density by V. Meyer's method, 5.05. It sublimes in colourless glistening needles, boils under 748 mm. at $257\text{--}260^\circ$, and can be partially distilled with steam. Its aqueous solution reacts neutral, causes a turbidity in basic and neutral lead acetates; with silver nitrate it gives a white flocculent precipitate, redissolved on warming: by adding ammonia to this and boiling, silver is deposited. Copper acetate forms a green flocculent precipitate, also redissolved on warming. The ferric chloride and ferrous sulphate reactions are especially delicate; the first gives a deep green coloration, which turns brownish-yellow on adding sodium carbonate; the second produces a reddish colour, and afterwards a black precipitate. It combines with both acids and metals. These latter compounds are very uninviting. The hydrochloride,

C_9H_7NO, HCl , forms yellowish glistening fibrous pointed needles, soluble in alcohol and water; the *platinochloride*, $(C_9H_7NO, HCl)_2, PtCl_4 + 2H_2O$, crystallises in clear yellow silky pointed needles, which lose their water of crystallisation at 100° , and are scarcely soluble in cold, but easily in hot water.

By oxidation with permanganate, α -hydroxycinchonic acid yields hydroxycinchomeronic acid, C_8H_5NO (this Journal, **38**, 406—409). The authors suggest the name *carbocinchomeronic acid*. From this result it follows that the sulphonic group in the α -cinchoninesulphonic acid, and the hydroxyl groups in the α -hydroxycinchonic acid and the α -quinophenol, are contained in the benzene nucleus.

According to Koenigs, there are 42 possible hydroxyquinoline-carboxylic acids; of these there are only two known, and they are the hydroxycinchonic acid made by Koenigs (this Journal, **36**, 471), and the α -hydroxycinchonic acid described in this paper. Kynuric acid probably is a third (Kretschy, this Journal, **38**, 44). The α -quinophenol is the first representative of the seven possible hydroxy-quinolines.

If sulphuric anhydride is allowed to act on the cinchoninesulphonic acid at 240° , a disulphonic acid is produced. This cannot be obtained if the tubes of cinchonic acid, phosphoric anhydride, and sulphuric acid are subjected to this temperature, for in this case besides the α -cinchoninesulphonic acid an isomeric acid easily soluble in water is formed.

D. A. L.

Pyridinecarboxylic Acids. By S. HOOGWERFF and W. A. VAN DORP (*Ber.*, **14**, 974).—The polybasic pyridinecarboxylic acids, which are decomposed by the action of heat, forming carbonic anhydride and a lower acid, undergo a similar change when boiled with glacial acetic acid. For example, tricarboxypyridic acid yields cinchomeronic acid; quinolinic acid forms nicotinic; and methylquinolinic gives methylpyridinecarboxylic acid.

W. C. W.

Isomerism in the Pyridine and Quinoline Series. By Z. H. SKRAUP (*Wien. Akad. Ber.*, **82**, 748—754).—The close connection between benzene and pyridine derivatives renders it very likely that the laws and regularities of the one series will apply very closely to the other also, as may be seen in the case of the three amidobenzoic acids compared with the three pyridinecarboxylic acids.

Amidobenzoic Acids.

1 : 2	1 : 3	1 : 4
145°	174°	186°

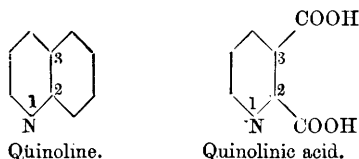
Pyridinecarboxylic Acids.

Picolinic	$134.5-136^\circ$
Nicotinic	$229.5-230$
γ -Pyridinecarboxylic	302.5

The analogy is further shown in the pyrrolcarboxylic acids, the synthetic acid being doubtless the *ortho*, as it splits up most easily into pyrrol and carbonic anhydride.

The two picolines again are probably ortho and meta, the former giving picolinic acid (b. p. 133·9°), the latter nicotinic acid (b. p. 140°).

It seems improbable that the cinchomeronic or pyridinedicarboxylic acid from the oxidation of quinolic acid has the constitution $[N : COOH : COOH = 1 : 2 : 3]$ assigned to it by Weidel and others, since the pyridinedicarboxylic acid obtained by Hoogewerff and by the author from the oxidation of *quinoline*, either synthetical, from coal oil or from cinchonine, appears to be identical with it, and from the direct formation of quinolic acid there is little doubt that the dicarboxylic acid has the constitution—



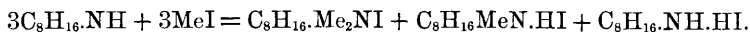
Such a dicarboxylic acid gives a possibility of three arrangements of the three mono-acids, corresponding to—

Nicotinic and picolinic acids.
 Nicotinic „ γ -pyridinecarboxylic acids.
 Picolinic „ γ -pyridinecarboxylic „

As quinolic acid is undoubtedly $[1 : 2 : 3]$, cinchomeronic acid must be $[1 : 2 : 5]$, as it yields γ -pyridinecarboxylic and nicotinic acids on heating. Wischnegradsky's ethylpyridine is probably a *meta*-derivative, as it yields *nicotinic* acid, which is also the case with the *iso*-cinchomeronic acid of Weidel and Herzig, and which may therefore be either $[1 : 3 : 5]$ or $[1 : 3 : 6]$. W. R. H.

Action of Heat on Ammonium Bases. By A. W. HOFMANN (*Ber.*, **14**, 705—713).—From the analyses of conine hydrochloride and hydrobromide, and the action of methyl iodide on conine, the author concludes that the formula of this base is $C_8H_{17}N$, as found by Blyth (*Annalen*, **70**, 73). *Conine hydrochloride*, $C_8H_{17}N.HCl$, is obtained as a white crystalline mass by passing hydrochloric acid gas into a solution of conine in anhydrous ether. *Conine hydrobromide*, $C_8H_{17}N.HBr$, is obtained by adding bromine to an ethereal solution of conine; a soluble substitution product is formed, and the hydrobromide separates out.

Methyl iodide reacts with conine in a manner similar to piperidine (*Ber.*, **14**, 659), thus—



Dimethylconylammonium iodide, $C_8H_{16}Me_2NI$, crystallises from alcohol in crystals melting at 100°. By silver oxide it is converted into the hydrate, which on distillation yields *dimethylconine*, $(C_8H_{15}Me)MeN$, a liquid boiling at 182°. Its *platinochloride*,



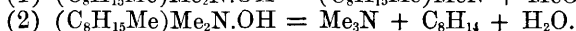
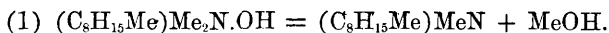
is sparingly soluble, and crystallises in slender needles, and melts below 100° to a deep red liquid.

Trimethylconylammonium iodide ($C_8H_{15}Me$) Me_2NI , is obtained by the action of methyl iodide on dimethylconine. It is easily soluble in water and alcohol, from which solutions ether precipitates it as an oil, solidifying after some time. The *platinochloride*,



is sparingly soluble in water, more soluble in alcohol, and crystallises in shining leaflets.

Trimethylconylammonium hydrate is decomposed by heat in a similar manner to the corresponding piperidine derivatives (*loc. cit.*), yielding dimethylconine and methyl alcohol, also trimethylamine, conylene, and water, thus:—

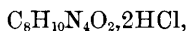


Conylene is a transparent, strongly refractive liquid (b. p. 125°). From experiment, its vapour density is 55.6 (C_8H_{14} requires 55). This hydrocarbon is identical with that discovered by Wertheim (*Annalen*, 123, 157; 130, 269).

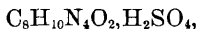
By the aid of the new formula for conine, the formation of azoconydrine is easily explained, namely, it is a nitrosoconine (C_8H_{16})'NON. It would also appear that conine is a homologue of piperidine. Kronecker finds that both these bases act on the nervous system, conine acting upon the motor, whilst piperidine acts on the sensitive nerves.
P. P. B.

Caffeine. By E. SCHMIDT (*Ber.*, 14, 813—817).—Caffeine saturated with hydrochloric acid gas and heated in sealed tubes at 240 — 250° for several hours, yields carbonic anhydride, and a residue containing ammonium chloride and methylamine hydrochloride. Heated with hydrochloric acid at 260° , caffeine undergoes partial carbonisation. Theobromine behaves very similarly to caffeine.

Salts of caffeine are formed only when concentrated acids react with the base; they are all decomposed by water, alcohol, and ether, and those salts with volatile acids are decomposed by exposure to the air. *Caffeine hydrochloride*, $C_8H_{10}N_4O_2.HCl + 2H_2O$, crystallises in colourless prismatic crystals. A hydrochloride having the formula



appears to be formed by the action of hydrochloric acid gas on the base; it loses a molecule of hydrochloric acid when kept over sulphuric acid. *Caffeine hydrobromide*, $C_8H_{10}N_4O_2.HBr + 2H_2O$, is obtained in colourless crystals. Caffeine appears to form two iodides, viz., $C_8H_{10}N_4O_2.HI$ and $C_8H_{10}N_4O_2.2HI$. *Caffeine nitrate*, $C_8H_{10}N_4O_2.HNO_3 + H_2O$, forms yellow thick needle-shaped crystals; like the above salts it is decomposed at 100° , yielding caffeine. *Caffeine sulphate*—



crystallises from a hot alcoholic solution in colourless, shining, needle-

shaped crystals. *Caffeine acetate*, $C_8H_{10}N_4O_2(C_2H_3O_2)_2$, forms colourless needles, decomposed by exposure to the air. *Caffeine normal butyrate*, $C_8H_{10}N_4O_2.C_4H_9O_2$, forms short white needles. The *isovalerate* has been obtained in colourless lustrous needles. The composition of the above salts, save the acetate and sulphate, appear to show that caffeine is a monacid base, a view which is supported by the composition of the auro- and platino-chlorides (Nicholson, *Annalen*, **62**, 71).

Caffeidine was prepared from caffeine by decomposing it with baryta; the aqueous solutions of its salts are decomposed by continued heating, forming ammonium and methylamine salts. *Caffeidine hydrochloride*, $C_7H_{12}N_4O.HCl$, crystallises in colourless needles, which are easily soluble in water.

The *platinochloride*, $(C_7H_{12}N_4O.HCl)_2.PtCl_6$, is formed by the spontaneous evaporation of its aqueous solutions in orange-yellow needle-shaped crystals. In some cases, it is obtained with 2 or 4 mols. H_2O . The *aurochloride* is very easily decomposed. Moist silver oxide decomposes caffeidine sulphate, forming amongst other products, ammonium and methylamine sulphates.

Caffeidine combines with ethyl iodide, forming *caffeidine ethiodide*, $C_7H_{12}N_4O.EtI$, and the base ethylcaffeidine also unites with ethyl iodide to form the iodide of a further ethylated base, hence it would appear that caffeidine is not a tertiary base like caffeine.

P. P. B.

Caffeine and Theobromine. By R. MALY and F. HINTEREGGER (*Ber.*, **14**, 723—728 and 893—897).—By the oxidation of caffeine with chromic mixture, cholestrophane is obtained, in quantities varying from 35.4—41.8 per cent.

Cholestrophane or *dimethylparabanic acid* is easily soluble in hot water, and at 20° 1 part is soluble in 53.4 parts of water. It crystallises from its aqueous solutions in thin rhombic tablets, or in leaflets (m. p. 145°). When heated with caustic alkalis, it is decomposed into oxalic acid and symmetrical dimethyl-urea, thus: $C_6H_8N_2O_3 + 2KHO = CO(NMeH)_2 + K_2C_2O_4$. That this urea is the symmetrical dimethyl-urea is shown by its melting point, viz., $97-100^\circ$ (according to Wurtz, 99.5°), and further by its yielding methylamine when heated with baryta-water.

Theobromine when oxidised in a similar manner yields *monomethylparabanic acid*, which is easily soluble in hot water, from which it crystallises in transparent prisms, m. p. 148° . Caustic alkalis resolve it into methyl-urea and oxalic acid, thus: $C_4H_4N_2O_3 + 2NaHO = NH_2.CO.NMeH + Na_2C_2O_4$.

In their second communication, the authors state that the complete products of the oxidation of caffeine are dimethylparabanic acid, ammonia, methylamine, and carbonic anhydride, $C_6H_{10}N_4O_2 + 3O = 2H_2O = C_5H_8N_2O_3 + 2CO_2 + NH_2Me + NH_3$; whilst theobromine yields monomethylparabanic acids, $C_7H_8N_4O_2 + 3O + 2H_2O = C_4H_4N_2O_3 + 2CO_2 + NH_2Me$ and NH_3 .

P. P. B.

Strychnine. By A. CLAUS and R. GLASSNER (*Ber.*, **14**, 773—778).—The authors find that different preparations of strychnine differ in

composition, and it may either have the formula $C_{21}H_{22}N_2O_2$ or $C_{22}H_{22}N_2O_2$; the free base melts at 284° , without decomposition.

Schützenberger (*J. pr. Chem.*, **75**, 122) found that by acting on strychnine salts with potassium nitrite, two bases are formed which he regarded as oxy-strychnines; these compounds have been obtained by the authors, who regard them as nitro-derivatives.

Dinitrostrychnine nitrate, $C_{22}H_{20}(NO_2)_2N_2O_2.HNO_3$, is obtained by passing nitric trioxide into an alcoholic solution of strychnine, or by boiling strychnine nitrate with concentrated nitric acid. It is soluble in alcohol and hot acetone, from which it crystallises in warty masses, is sparingly soluble in water, and insoluble in ether and chloroform.

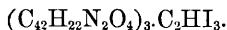
Dinitrostrychnine, $C_{22}H_{20}(NO_2)_2N_2O_2$, is obtained by adding ammonia to the nitrate, it crystallises from alcohol in orange-yellow leaflets, which darken on exposure to the air, m. p. 226° . It is insoluble in all ordinary solvents save alcohol. Its platinochloride is obtained as a yellow precipitate, which is easily decomposed. It is easily reduced, forming unstable compounds.

Cacostrychnine, $C_{21}H_{14}(NO_2)_3N_2O_4$, is obtained by treating an aqueous solution of strychnine nitrate with nitric acid; its formation is attended with evolution of carbonic anhydride. It is sparingly soluble in the ordinary solvents, more soluble in hot acids, and from boiling nitric acid it crystallises in golden-yellow needles, united concentrically in groups, and from concentrated solutions in yellow hexagonal tablets. It dissolves in alcoholic potash, forming violet solutions, and in aqueous potassium hydroxide to red solutions.

By reducing agents, it is converted into colourless compounds, which oxidise rapidly in the air. The existence of three nitro-groups is shown by the modification of Limpricht's method, used in the analysis of dinitrobrucine (p. 749).

P. P. B.

A Compound of Strychnine with Iodoform. By LEXTRAIT (*Compt. rend.*, **92**, 1057—1059).—The author has obtained a compound of strychnine with iodoform of the composition—

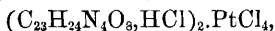


It is best obtained by dissolving 5 grams of crystallised iodoform, and 12 grams of strychnine in 500 c.c. of alcohol at 85° , and allowing the mixture to cool in a closed vessel. After about 24 hours, the crystals are filtered off, and washed with a small quantity of alcohol; then rapidly pressed between filter-paper, and finally dried, protected from light and air. The compound is very unstable. It is decomposed by light, iodoform being eliminated. It is not soluble in either hot or cold water, but readily dissolves in ether and chloroform. A litre of 98 per cent. alcohol dissolves 3.40 grams at 15° . It is decomposed by dilute acids, iodoform being set free, and salts of strychnine formed. On heating to 90° , it begins to decompose, and at 130° it blackens. When it is boiled with water, iodoform distils off. Alcohol partially decomposes it, and hence cannot be employed as a crystallising medium.

Quinine appears to form a similar compound with iodoform.

J. I. W.

Brucine. By A. CLAUS and R. RÖHRE (*Ber.*, **14**, 765—773).—*Dinitrobrucine*, $C_{23}H_{24}(NO_2)_2N_2O_4$.—This compound is obtained by passing nitric trioxide into an alcoholic solution of brucine; brucine nitrate separates out at first and again dissolves, forming a red solution, from which the dinitrobrucine separates as a heavy, granular, blood-red precipitate. By washing with alcohol and ether, it is obtained as an amorphous, vermilion, velvety-lustrous powder. It is easily soluble in water, sparingly in alcohol, and insoluble in ether. By treatment with ammonia and other bases, it is decomposed, forming coloured unstable compounds. The *platinoclchloride*—



is obtained as a yellow precipitate, on adding platinic chloride to the aqueous solution of dinitrobrucine. By reduction, it is converted into colourless compounds, which are very unstable. In estimating the NO_2 -groups in dinitrobrucine by Limpricht's method (this Journal, **34**, 335), the titration with iodine solution is continued until a drop of the solution no longer gives a brown precipitate with sulphuretted hydrogen. In this manner the presence of two nitro-groups has been demonstrated.

Cacoteline, $C_{20}H_{22}(NO_2)_2N_2O_6$, also yields unstable compounds when reduced; but by the above modification of Limpricht's method, the presence in it of two nitro-groups has been shown.

The authors have been unable to confirm Sonnenschein's statement (*Ber.*, **8**, 212) that strychnine is formed by the action of dilute nitric acid on brucine; chromic acid has no action on brucine; and further, the compound of brucine and methyl iodide, when heated with potassium hydroxide, yields a resinous product.

Brucine dried at 150° melts at 178° , forming a colourless liquid.

P. P. B.

Test to Distinguish Ptomaines from Vegetable Alkaloids.

By P. BROUARDEL and E. BOUTMY (*Compt. rend.*, **92**, 1056).—The authors find that potassium ferricyanide forms a convenient reagent for distinguishing ptomaines (alkaloids extracted from a dead body) from vegetable alkaloids, inasmuch as the former reduces it, whilst the latter exerts no action on it. In order to test a base extracted from a body in cases of suspected poisoning, the authors convert it into sulphate, and add a few drops of the solution to a small quantity of ferricyanide in a test-tube; on adding neutral ferric chloride, if a ptomaine be present, Prussian blue will be formed; but if the base is a vegetable alkaloid, no reaction occurs.

Morphine and veratrine, however, form exceptions to the rule.

J. I. W.

Oxidation of Cholic Acid. By P. T. CLÈVE (*Bull. Soc. Chim.* [2], **35**, 373—379 and 429—433).—On oxidising cholic acid with permanganate, the author finds that two acids are produced. One is precipitated from the aqueous solution on adding dilute sulphuric acid; the other, oxalic acid, remains in solution. The author finds that the latter is not formed in sufficient quantity to warrant the conclusion that it is produced by the direct oxidation of the cholic acid. He finds that the other acid is only obtained in a crystalline state, when the

action of the permanganate is prolonged. He allows it to extend over several weeks. The acid which is then obtained crystallises from water in scales or brilliant rhombic prisms.

By acting on cholic acid with chromic mixture, the same acid is obtained. The author believes, however, that a second new acid is formed in the reaction, but in such small quantity that he has been unable to obtain it pure. He was unable, by oxidising cholic acid by Tappeiner's method, to obtain the cholesteric acid described by that chemist, but he obtains the above new acid. He also did not find acetic or any fatty acids among the products of oxidation, although when cholic acid is crystallised from alcohol, the crystals appear to occlude small quantities of the liquid, and this on oxidation yields acetic acid and aldehyde. The main product consisted of a resinous substance, which on treating, according to Tappeiner's method, yielded cholanic acid and the above new acid, which the author calls *bilianic acid*. The latter has not the same bitter taste as cholic acid, and does not give the Pettenkofer reaction. It is easily soluble in alcohol and in acetic acid; it separates from a solution of the latter on cooling in a soapy mass, which after a short time becomes transformed into rhombic crystals 5—6 mm. long. The rotatory power of the acid crystals containing $4\text{H}_2\text{O}$ is $[\alpha] = 47.4^\circ$. The calcium salt, $\text{C}_{50}\text{H}_{66}\text{Ca}_3\text{O}_{18} + 5\text{H}_2\text{O}$, is obtained by treating the acid with milk of lime. It is soluble in cold water, but on warming, the solution deposits small needles, which disappear as the liquid cools. The barium salt, $\text{C}_{50}\text{H}_{66}\text{Ba}_3\text{O}_{18} + \text{H}_2\text{O}$, crystallises from very concentrated solutions in spheroidal masses of transparent prisms. The normal lead salt, obtained by precipitating with acetate of lead, crystallises in microscopic scales or tables. The acid lead salt is obtained by adding lead nitrate to a warm saturated solution of the acid in dilute ammonia. It forms brilliant hexagonal plates. The neutral silver salt is precipitated when silver nitrate is added to a solution of the calcium salt. It forms white microscopic scales. The acid silver salt is obtained in a similar manner to the lead salt. It forms colourless needles.

Cholanic Acid.—Tappeiner gave to this acid the formula $\text{C}_{20}\text{H}_{28}\text{O}_6$. The author has prepared the free acid and some of its salts, and finds that his analyses, as well as those of Tappeiner, accord very well with the formula $\text{C}_{24}\text{H}_{36}\text{O}_7$. The acid is tribasic. The author was unable to prepare the acid barium salt mentioned by Tappeiner.

J. I. W.

Papaine; a New Contribution to the History of Soluble Ferments. By A. WURTZ (*Compt. rend.*, 91, 787—791).—It has been already shown that papaine, the soluble ferment of the *Carica papaya*, is closely connected with the albuminoids, both in its composition and chemical properties; further researches having been made, the author is now able to give some details regarding its digestive power, and to express an idea as to its mode of action.

0.1 gram of papaine was digested with 100 grams of moist fibrin, diffused in 500 c.c. of distilled water to which a few drops of hydrochloric acid were added. At the end of 36 hours, there was obtained from the mixture 2.5 grams of insoluble dyspeptone; 8.9 grams of parapeptone precipitable by alcohol; and a brown residue after eva-

poration weighing 10·3 grams. This residue when taken up again by water, no longer gave a precipitate on addition of nitric acid; but on careful evaporation and standing, it eventually deposited crystals, which, after purification, presented the appearance of leucine.

From this experiment, it is evident that the papaine had dissolved 1000 times its weight of moist fibrin, of which the largest portion had been transformed into peptone not precipitable by nitric acid, and that, in consequence of the complete hydration of the fibrin, it had even formed a small quantity of an amido-body, the same being known to occur in the process of good peptic digestion.

In another experiment, 0·05 gram of the same papaine liquefied 100 grams of moist fibrin, or 2000 times its weight, with the exception of a small residue of dyspeptone weighing 4·2 grams. In order to ascertain if the ferment was capable of assimilating water itself, a solution of 3 grams of papaine in 20 c.c. of water was heated for 15 days to 50°; after filtration and evaporation in a vacuum, it was precipitated by alcohol, and the modified papaine thus obtained was submitted to analysis. As was anticipated, the ferment had undergone partial hydration, in such a manner that its carbon was lowered by about 2 per cent. Several similar experiments were made at various temperatures with like results, the extent of the hydration appearing within certain limits to proceed *pari passu* with the temperatures.

The following experiment may, perhaps, throw some light upon the mode of action of the papaine. 0·3 gram was dissolved in 50 c.c. of water, and 10 grams of fibrin digested with the solution, and at the end of 20 minutes the liquid was expressed, and the fibrin subjected to prolonged washing with cold water. In the liquid obtained by the expression of the fibrin a new portion of 15 grams was digested, and at the expiration of half an hour this second portion of fibrin was expressed, and washed as the first. Both portions (the first reduced to 7 grams by the beginning of digestion, the second to 14 grams) were digested at 40° with pure water, when both became dissolved, the second leaving a residue of 4 grams of moist dyspeptone.

In these two experiments, the washings had certainly removed the *dissolved* ferment, and the washed fibrin would not have been able to dissolve, except by the action of a portion of the ferment fixed upon, or perhaps combined with it; the ferment fixed upon the fibrin in an insoluble state had then redissolved it, in consequence of the hydration of the fibrin.

By the above and similar experiments it was sought to establish that the papaine begins by combining with the fibrin, and that the insoluble product then gives by the action of water the soluble substances resulting from the hydration of the fibrin; at the same time, the ferment, being again set free, is necessarily at liberty to exercise its action on a new portion of fibrin.

J. W.

Blood-crystals. By H. STRUVE (*Ber.*, 14, 930—932).—Freshly prepared blood-crystals which have been rendered insoluble by treatment with alcohol, are decolorised by ammonia or by chlorine-water without undergoing any change in their crystalline form. Hence the

author concludes that the blood-crystals consist essentially of globulin mixed with a minute quantity of the red colouring-matter of the blood.

W. C. W.

Physiological Chemistry.

Influence of Alcohol, Beer, and Wine on Digestion. By R. FLEISCHER (*Bied. Centr.*, 1881, 12).—Alcohol merely retards the solution of albumen by pepsin in presence of hydrochloric acid, the retardation increasing with amount of alcohol. With beer and wine, the solution is very slow indeed, and, in some cases, does not take place at all. In the human subject digestion is, with a moderate amount of wine, &c., in the stomach, hardly at all retarded, because the fluids are so rapidly absorbed. E. W. P.

The Influence of Malt Liquids on Digestion. By F. EMKEN (*Bied. Centr.*, 1881, 63).—Dried bread is to a certain extent soluble in alkaline water and "soda-water," but beer exerts a greater solvent action. The removal of carbonic acid from beer does not affect its solvent action, but boiled beer and beer containing salicylic acid act but feebly, whilst if lactic acid is present, the solvent power is greater. E. W. P.

Influence of certain Salts and Alkaloids on Digestion. By L. WOLBERG (*Bied. Centr.*, 1881, 62).—Chlorides, sulphates, and nitrates of potassium, sodium, and ammonium retard digestion. Anhydrous salts hinder fermentation more than hydrous salts. Digestion is also retarded by alkaloids, morphine, narcotine, &c. (except quinine). E. W. P.

The Influence of Food on the Constitution of the Fat of Animals. By A. MUNTZ (*Bied. Centr.*, 1881, 26).—The constitution of the fat varies with the breed, the age, and the part of the animal examined. To obtain an idea of the influence exerted by food on various animals as regards the fat, sheep (Southdowns) were fed on bran, maize, and oil-cake: also the influence of race was studied by examination of the fat of various oxen, cows, and pigs. As regards the experiments on sheep, the results obtained are shown in the following table:—

	Weight.	Fat from entrails.			Fat from ribs.		
		M. p. of fatty acids.	Per cent.		M. p. of fatty acids.	Per cent.	
			Solid acid.	Fluid acid.		Solid acid.	Fluid acid.
	kilos.						
Store feeding	49	49·2°	74	26	44·7°	52	48
Maize.....	61	46·7	60	40	40·2	38	62
Bran	58	45·9	56	44	35·7	26	74
Oil cake.....	57	46·5	58	42	39·5	35	65

The fat from a sheep under normal conditions is therefore richer in solid fatty acids than that from a fattening sheep. The ratios of the acids present were estimated by means of Chevreul's tables of the melting points of the mixed acids after saponification of the fat.

E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Constancy in Composition of Plants. By H. PELLET (*Bied. Centr.*, 1881, 67).—Analyses of *Soja hispida* from different sources shows that the composition of the whole seed and of the ash is very constant, the alkalis being the only substances liable to vary.

E. W. P.

Composition of Protoplasm. By RODEWALD and J. REINKE (*Bied. Centr.*, 1881, 32).—The material employed consisted of the spores of the *Aethalium septicum*. Besides water and an albuminoid resembling fibrin capable of being separated by pressure from the liquid part of the protoplasm, and which has been called *Plastin*, there occur these following substances:—Vitellin, myosin, peptone, peptonoid, pepsin, nuclein (P), lecithin, guanine, sarcine, xanthine, ammonium carbonate, paracholesterin, cholesterin (traces), aethalium resin, yellow colouring-matter, glucoses, saccharose, olein, stearin, palmitic, butyric, carbonic acids, fatty acid glycerides, fatty acid paracholesterides, calcium stearate, palmitate, oleate, lactate, oxalate, acetate, formate, phosphate, carbonate, and sulphate, magnesium and potassium phosphate, sodium chloride, and iron.

E. W. P.

Chemical Composition of Linseed. By A. LADUREAU (*Ann. Agronomiques*, 6, 215—223).—The linseed sown in France is imported from Russia. The seed from the first year's crop may be sown in the second year; but the second year's seed is no longer of any use for the production of a fresh crop, the plant from it being short, poor, etiolated, and of scarcely any value. The second year's seed is there-

fore used only for making oil. These deteriorated seeds are not distinguishable in appearance from the Russian seed, and the author therefore undertook a series of analyses to ascertain whether any chemical distinction could be established, and whether the addition of any ingredient to the soil would enable the French to become independent of imported seed. No distinction was established in the organic constituents of the various seeds, and the ash from 31 samples of seed was therefore analysed with great care. Twelve of these were from Russia, three from the north of France (1st crop), four from the north of France (2nd crop), the rest from India, Chili, Algeria, Oran, Danubian Principalities, Roumelia, European Turkey, and Bayonne. The mean of the 31 analyses of ash is as follows:—Potash, 8.45; chlorine, 0.43; sulphuric acid, 4.45; phosphoric acid, 4.60; soda and carbonic acid, 3.76 (= 24.10 soluble in water); lime, 7.30; magnesia, 18.00; phosphoric acid, 27.00; sulphuric and carbonic acids, 23.43 (= 71.00 soluble in dilute nitric acid); silica and insoluble matter, 4.80, in 100 parts. The mean percentage of ash was 3.60. The percentage of ash, and in the ash the percentage of insoluble matter and the proportion of soluble to insoluble salts, vary very little. The potash, lime, and magnesia vary slightly in the different samples. The greatest variation is in the total phosphoric acid, which in the imported seed amounts to 40 per cent. of the ash, in the first seed crop grown from this to 30 per cent., and in the second year's seed to 15—20 per cent. In consequence of this result, plots of ground were manured with phosphatic and other manures, and the first year's crop of seed from each analysed. The results are tabulated in the paper, but do not suggest any general conclusion. The experiments will be continued with the second year's and following crops.

J. M. H. M.

Composition of Wheat Ashes. By F. MEUNIER (*Ann. Agronomiques*, 6, 252—261).—Whilst most chemists, including Boussingault and Fresenius, have found only a very small quantity of ferric oxide in the ashes of wheat, Gasparin (*Mémoires de la Société Centrale d'Agriculture*, 1875, 267) has found as much as 20.68 per cent., or one-fifth of the entire ash. At the same time the phosphoric acid found by him is 11 per cent. under that given by most other chemists. The author has determined the iron and the phosphoric acid each by three different analytical processes, the results being practically identical. The iron was determined (1) directly in the solution of ash by titration with potassium permanganate; (2) by precipitation and weighing as ferric phosphate; and (3) by dissolving the precipitated phosphate, and titrating with potassium permanganate. Process (2) gives results a shade higher than (1) and (3), on account of a minute quantity of aluminium phosphate contained in the ferric phosphate precipitate. The phosphoric acid was determined gravimetrically as uranic phosphate, gravimetrically as magnesium pyrophosphate after two precipitations, and volumetrically by solution of the ammonium magnesium phosphate precipitate and titration by uranic acetate, according to Joulie's method.

Full details of the analytical methods are given in the paper.

The following table gives the mean results:—

Variety.	Ferric oxide.	Phosphoric acid.
Hunter	1.20	48.64
Richelle, white Naples	1.75	49.26
Chiddam, spring wheat.....	0.97	48.82
White petanielle.....	1.44	49.04
Saumur spring wheat	0.69	49.32
Smyrna	0.90	49.03
Bergues	1.35	49.08
Saumur autumn wheat	0.72	49.25
Mean	1.11	49.05

Complete analysis of the ash of Saumur wheat yielded the following result:—

K ₂ O.	CaO.	MgO.	MnO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
28.58	3.06	15.37	0.09	0.70	49.34	trace	1.85	trace

The author concludes that the oxide of iron weighed by Gasparin was a mixture of ferric oxide with aluminium phosphate, and cites an experiment in support of this statement. J. M. H. M.

Clover Sickness. By S. LINDE (*Bied. Centr.*, 1881, 5—11).—The author holds with Kühn, and in opposition to Liebig, that clover sickness is due to parasites in the soil; but he adduces no positive evidence of his assertion, although he has found *Pleospora herbarum* in dead clover roots. Two sets of field experiments were conducted for twelve years; in the first set clover was grown without intermission for twelve years, and in the other clover alternated with other field crops according to the Norfolk system. In both sets there were unmanured plots, the others being manured with stable dung, gelatin, &c. In the first set it was found that manuring (when considering the average yield) had but little influence, and that in all cases clover sickness was apparent after a certain time; in the case of the unmanured plot, it seemed to disappear after ten years; also it was found that whereas the unmanured plot required to be re-sown every three years, it was necessary to re-sow the others every two years. The yield on all the "rotation" plots was much higher than on the "continuous" plots. Sickness was not visible: but heavy manuring in the first case appeared to produce a greater amount of sickness by causing a greater yield of clover; hence a larger amount of residue in the soil, which produced a correspondingly larger number of parasites. E. W. P.

Spring Barley as Green Fodder. By I. PIERRE and LEMETAYER (*Ann. Agronomiques*, 6, 261—262).—Instead of employing green rye as a fodder crop, many of the small farmers and dairymen in the neighbourhood of Paris grow spring barley for this purpose, as it is more tender and better liked by cattle. The authors have analysed the plant at various stages of growth with the following results:—

Date.	Total weight per two square metres.	Moisture.	Dry matter.	Nitrogen per cent. of green crop.	Nitrogen per cent. of dry matter.
	kilos.	per cent.	per cent.		
29th April, 1878.....	5·03	94·25	5·75	0·284	2·13
16th May, „	6·02	88·61	11·39	0·252	1·29
31st May, „	5·04	80·60	19·40	0·241	9·6
15th June „	3·70	78·52	21·48	0·188	6·7

J. M. H. M.

On Swedes. By E. PHILIPPAR (*Ann. Agronomiques*, 6, 205—215). Swedes are grown largely in Brittany, the climate and soil of that district being very suitable to their commercial cultivation. The light recently formed granitic soils pass through two distinct periods in respect to the cultivation of root crops. During the first period the soil is acid, friable, and contains much humus, and for eight or ten years it produces large crops of swedes, but will not grow beet. Having by this time lost a part of its organic matter and consequent acidity, it becomes suitable for the cultivation of beet and of general farm crops, but will not grow swedes. The experiments detailed in the present paper were undertaken to determine the comparative yield of the different varieties and their composition and nutritive value.

Comparative yield.—Samples of all the varieties sold in 1879 by Messrs. Vilmorin, were sown side by side in experimental plots, and received exactly similar treatment, the crops being lifted simultaneously on June 2, 1880. The minimum temperature recorded to that date was -11°C . The results, translated approximately into tons per acre, are as follow :—

Name.	Yield. Tons per acre.	Remarks.
1. White turnip (5740)	14 $\frac{1}{2}$	Underground. Frozen.
2. Sutton's Champion swede (5920) ...	11 $\frac{2}{10}$	Roots regular, very fine.
3. White red topped turnip (5760)	10 $\frac{8}{10}$	Underground. Neck much developed.
4. Yellow swede (5820)	8 $\frac{1}{2}$	
5. Early yellow swede (5963)	6 $\frac{2}{10}$	Very early and hardy.
6. Laing's yellow purple topped swede (5883)	6 $\frac{1}{2}$	A little frozen.
7. Purple kohl-rabi (6041)	6 $\frac{1}{2}$	A little frozen.
8. White kohl-rabi (6004)	5 $\frac{2}{10}$	Very little frozen.
9. Yellow red-topped swede (5840)....	5 $\frac{1}{10}$	
10. Vienna early white kohl-rabi (6015)	3 $\frac{7}{10}$	Much frozen.

Composition and Nutritive Value.—In order to ascertain the comparative weights of dry nutritive material yielded per acre, determinations were made of the water, ash, and nitrogen in the different roots. The results are embodied in the annexed table, in which the roots are

arranged in order of the *yield per acre* of dry proteïds (nitrogen $\times 6.25$):—

	Specific gravity.	Water per cent.	Ash per cent.	Nitrogen per cent. of dry matter.	Lbs. per acre of albuminoids.
1. Sutton's Champion swede....	0.984	87.0	0.640	1.793	479
2. White turnip.....	0.957	90.2	0.896	2.413	472
3. White kohlrabi	0.902	86.4	3.098	3.244	363
4. White red-topped turnip ...	0.943	91.0	0.438	2.206	300
5. Yellow red-topped swede ...	0.957	90.2	0.562	3.448	278
6. Early yellow swede.....	0.971	90.4	0.334	2.206	205
7. Purple kohlrabi	0.953	91.0	0.650	2.551	201
8. Yellow swede	0.962	91.0	0.446	1.862	194
9. Vienna early white kohlrabi.	0.911	90.2	0.872	3.724	170
10. Laing's yellow swede.....	0.956	91.6	0.490	1.931	156
11. Smooth white (short leaved) turnip.	0.988	88.0	0.484	2.068	152

Two experiments with artificial manures are recorded in the paper. The unmanured soil yielded 7 tons 13 cwt. per acre of mixed varieties of swedes; with an application of 743 lbs. per acre of ammoniacal salts (containing 10 per cent. nitrogen), the yield was increased to 12 tons 19 cwt.; with 743 lbs. nitrogenised superphosphate (containing 3 per cent. nitrogen and 10 per cent. P_2O_5) the yield was 8 tons 5 cwt.

J. M. H. M.

Analysis of Beet Seeds. By H. PELLET and M. LIEBSCHNITZ (*Bied. Centr.*, 1881, 35—37).—By carefully rubbing the seeds of various sorts, the husk was separated from the kernel, and the two were submitted to a full analysis, the details of which are given. The husks appear to contain thrice the quantity of ash that the kernel does, whilst the fat and starch is greatest in the kernel.

E. W. P.

Comparison of "Diffusion" and "Press" Residues as Foods. By SIMON-LEGRAND (*Bied. Centr.*, 1881, 28).—Forty cattle were fed with "diffusion" residues and forty more with "press" residues for 94 days, the gain per head being in the first case 90.57 kilos., and in the second case 85.13 kilos. The comparison is, therefore, favourable to the "diffusion" residue.

E. W. P.

Note by Abstractor.—These experiments corroborate the conclusions drawn from analyses of the two foods (see this vol., p. 301).

Composition of Brandy Distillery Residues. By DE LEUW (*Bied. Centr.*, 1881, 42).—The composition of most artificial feeding stuffs is constant within certain limits, but the above residues are very variable in composition, which depends on the degree of fermentation, &c. To enable the buyer to judge of the amount of material to give as food (for the water varies from 92—87, and dry matter from

8—13 per cent.), the following method of calculation is recommended :—Add together the constituents of the materials employed in the distillery (maize, &c.), subtract from the sum the quantity of starch which is converted into alcohol (1 kilo. starch producing 716 c.c. absolute alcohol); divide the result by the number of litres of “grains” purchased, and the quotient is the composition of 1 litre.

E. W. P.

American Flesh-meal for Milch Cows. By M. SCHRODT and H. v. PETER (*Bied. Centr.*, 1881, 29—32).—The experiments on two cows were continued over 89 days divided into four periods, and during those periods the cows were fed with a mixture of hay, roots, bran, rape cake, and to this was added in the 2nd and 3rd periods starch and flesh-meal; the daily ration and nutrient ratio of the foods were during—

		Dry matter.	Nutrient ratio.
Period	I	9·8 kilos.	1 : 4·8
	„ II	9·81 „	1 : 4·3
	„ III ..	10·15 „	1 : 4·3
	„ IV	9·80 „	1 : 4·8

Flesh-meal increased the yield of milk and of fat, although the percentage of fat was not increased; compared with oil cake and other nitrogenous foods employed, there was a saving of 2 per cent. a head per diem; the taste of the milk and butter was not affected.

E. W. P.

Comparative Experiments on the Manurial Values of Soluble, Reduced, and Precipitated Phosphates, on Sandy Soils. By C. MÜLLER and W. C. MÜLLER-SCHEESEL (*Bied. Centr.*, 1881, 21—24).—Seven plots of 1 morgen were selected for the growth of oats on a light soil, which for ten years previously had been grazed by sheep. Plots 1 and 7 were unmanured, and the others were manured with 15 lbs. nitrogen as Chili saltpetre, and in addition as follows:—(2) 30 lbs. *soluble phosphoric acid*; (3) 30 lbs. phosphoric acid, of which 11 lbs. were soluble, and 19 lbs. reduced; (4) 11 lbs. soluble phosphoric acid; (5) 30 lbs. phosphoric acid as precipitated phosphate. The results of the harvest show that in a pecuniary way there was a great gain in manuring. Plots 2—5 show increase of yield by phosphates over nitrogen only. Plots 2 and 5 show that both the yield of grain and straw is increased by soluble over insoluble phosphates. From plots 3 and 4 we gather that reduced phosphates are of great advantage, to the amount of 14 per cent. above that quantity produced by soluble phosphates only; and it is evident from the examination of plots 2 and 3 that the partial substitution of a soluble, by a reduced phosphate, exercises a beneficial effect on the yield of grain, to the amount of 5 per cent., the straw and chaff remaining about the same in both cases.

E. W. P.

African Guano. By A. PETERMANN (*Bied. Centr.*, 1881, 12).—The following analysis represents the composition of a South African

guano imported into Belgium from Halifax and Ichaboe Islands, &c. :—

H₂O = 21·66, organic matter and ammonia salts 44·89 (N as NH₃ = 4·57, N in other forms 9·20), K₂O = 2·00, Na₂O 4·25, CaO = 8·18, MgO = 0·60, Fe₂O₃ = 0·14, P₂O₅ = 2·85; P₂O₅ (soluble in acids), 5·95, SO₃ = 0·43, Cl 1·76, SiO₂ 7·69. The guano is dry, fine, light brown, contains feathers and friable crystalline lumps, and the ash is white. The portion insoluble in acid consists of quartz, mica, and fragments of diatoms.

E. W. P.

Analytical Chemistry.

Use of Potassium Permanganate in Volumetric Analysis. By C. ZIMMERMANN (*Ber.*, **14**, 779—782).—In titrating with potassium permanganate the author finds that the inaccuracy due to the presence of hydrochloric acid may be avoided by adding a solution of manganese sulphate. 20 c.c. of a solution of manganese sulphate, containing 1 gram of the salt in 5 c.c. of water, is sufficient to insure accuracy in the titration of iron by permanganate, even in presence of 50 c.c. of free hydrochloric acid (sp. gr. 1.12). The above holds for the titration of uranous salts also. P. P. B.

Influence of Ammonia on the Estimation of Bicalcium Phosphate. By A. KÖNIG (*Bied. Centr.*, 1881, 59—61).—Petermann recommends the addition of ammonia to the citrate solution, but this addition considerably reduces the amount of phosphate dissolved. The same holds good if superphosphates are employed. When also the phosphoric acid is estimated in the alkaline citrate solution by magnesia mixture, part of the lime is carried down and estimated as magnesium pyrophosphate; the lime thus carried down is generally 2—3 per cent. of the precipitate. Some of the phosphate remains in solution, and is not precipitated by magnesia. E. W. P.

Action of Citric Acid on Phosphates. By A. GRUPE and B. TOLLENS (*Ber.*, **14**, 754—758).—In this Journal (**38**, 825) an account is given of the action of ammonium citrate on phosphates: the authors propose to replace this reagent by a 0.25 per cent. solution of citric acid. This solution dissolves dicalcium phosphate, ammonium magnesium phosphate, iron and aluminium and also tricalcium phosphates. It dissolves about 11.6 per cent. of bone earth, and amounts of the natural phosphates varying with their nature. Water containing carbonic anhydride behaves in a somewhat similar manner, dissolving 8.25 per cent. of phosphoric acid in tricalcium phosphate, and 16.25 per cent. of the acid in dicalcium phosphate.

To estimate the phosphate dissolved out by ammonium citrate or citric acid, the solution is evaporated to dryness with lime, and the product ignited to remove organic matter. The ignited mass is treated

with water and nitric acid, and the phosphoric acid removed by molybdic acid. The phosphoric acid dissolved by citric acid may be directly precipitated by molybdic acid, and estimated as magnesium ammonium phosphate.

P. P. B.

Direct Estimation of Alumina in Presence of Iron. By E. DONATH (*Wien. Akad. Ber.*, **82**, 729—732).—This method depends on the fact that aluminium does not form compounds with cyanogen, like iron.

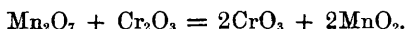
When solutions of aluminium containing iron in the ferrous state are treated with excess of potassium cyanide and a little potassium hydroxide, the brown precipitate of ferrous oxide and cyanide is completely redissolved, with formation of potassium ferrocyanide.

A conveniently small known volume of the concentrated solution is nearly neutralised with ammonia, and the iron completely reduced with sodium thiosulphate solution. It is then slowly added to a hot slightly ammoniacal solution of potassium cyanide (containing about 15 to 20 grams KCy to 0.1 to 0.3 gram FeO. The solution is cooled as rapidly as possible, rendered acid with acetic acid, and ammonium carbonate is added in slight excess. The precipitated alumina is generally white, and may be treated as usual.

The trial analyses are satisfactory.

W. R. H.

Volumetric Determination of Chromium and Manganese in presence of Ferric Oxide and Alumina. By E. DONATH (*Ber.*, **14**, 982—983).—When a neutral solution containing chromium sesquioxide is added to a hot solution of potassium permanganate which has been rendered strongly alkaline by the addition of sodium carbonate and hydroxide, the chromium sesquioxide is oxidised to chromic acid,



The reaction is complete when the purple colour of the permanganate is destroyed.

On the addition of a manganous salt to a hot alkaline solution of permanganate, the following reaction takes place: $3\text{MnO} + \text{Mn}_2\text{O}_7 = 5\text{MnO}_2$. Since these reactions are not interfered with by the presence of ferric oxide and alumina, they may be advantageously used in the volumetric estimation of chromium and manganese.

W. C. W.

Separation of Silver from Lead. By E. DONATH (*Wien. Akad. Ber.*, **82**, 733—735).—This method depends on the fact that ammoniacal silver solutions, heated to the boiling point with glycerol, are not changed, but on adding sodium or potassium hydroxide the silver is precipitated as a fine grey powder or mirror, this reaction being very delicate. Lead solutions under the same circumstances are quite unaltered on boiling.

The nitric acid solution of the two metals is treated with 4—5 c.c. pure glycerol, a slight excess of ammonia solution, and 10—15 c.c. concentrated potassium or sodium hydroxide, whereby a clear solution is obtained. On heating for 3—5 minutes to the boiling point, all

the silver will be thrown down, and should be washed with hot dilute acetic acid.

The separation is equally good in the presence of bismuth and copper.

W. R. H.

Quantitative Estimation of Dust in Workshops. By W. HESSE (*Dingl. polyt. J.*, **240**, 52—55).—By means of an aspirator the air to be examined was sucked through a small glass tube filled with cotton-wool. A gas meter was placed between the aspirator and the glass tube. Before and after the operation the glass tube and the contents are dried in a desiccator over sulphuric acid, and the difference in weight after the operation shows the quantity of dust present in a certain volume of air. Thus the author has analysed the air of works of different design, and the results, which are tabulated in the original paper, seem to show that in some cases air may be contaminated largely with dust without injuriously affecting the workmen, *e.g.*, in corn-mills, ironworks, &c.; whilst in other cases, such as mechanical weaving, brush-making, cutting off the long hairs of skins, and similar operations, the air may contain less dust, and yet have a serious influence on the health of the men. Moreover, it is most important to ascertain whether or not the dust in the air to be inhaled acts on the organism.

D. B.

Detection of Logwood in Wine. By A. PIZZI (*Gazzetta*, **11**, 120—124).—When a solution of logwood is treated with manganese dioxide, it becomes brown, and this brown liquid by the action of zinc and hydrochloric acid gives a colourless solution of hæmatoxylin; this may be detected by the ordinary reagents for that substance, alkalis and their carbonates giving a blue-violet coloration; calcium hydroxide a red-violet; tin dichloride or ammonium molybdate in a solution slightly acid with nitric acid, a violet coloration. Advantage has been taken of this reaction for the detection of logwood in wines; 20 c.c. of the wine is agitated with 2 grams finely powdered manganese dioxide, filtered, and the brown liquid treated with zinc and hydrochloric acid, which reduces the oxidised logwood colouring matter to hæmatoxylin. The solution is then divided into several portions, and tested with the reagents given above. The author has examined wines to which other red colouring matters have been added, and although these yield brown solutions with manganese dioxide, the reduced solution does not give the hæmatoxylin reactions; Brazil wood is the only one which has any analogy with logwood, but here also there are differences. The author is investigating a method for distinguishing it from logwood.

C. E. G.

Asparagine. By F. MEUNIER (*Ann. Agronomiques*, **6**, 275—281).—The author finds that the determination of asparagine by the method of Sachs and Kormann, depending on the measurement of the nitrogen evolved by the action of nitrous acid, is inaccurate. He has devised the following process, which depends on the production of potassium aspartate and ammonia, when asparagine is treated with potassium hydroxide. The crushed, dried, and weighed substance is placed in a little bag with meshes small enough to retain the starch; this is placed

in a porcelain dish, exhausted with boiling water, the filtered solution is heated with subacetate of lead to precipitate albuminoids and leucine, and the excess of lead is removed from the filtrate by sodium hydrogen carbonate. The filtrate from the lead carbonate is distilled with potassium hydroxide, and the ammonia collected and titrated as in Schloesing's method. When ammonium salts are present, they must be separately estimated. The author has experimented on the germination of peas and beans in water, in light and in the dark, and has verified by the above method of estimation, (1) that the amount of asparagine formed varies with the duration of growth and the nature of the seed; (2) that in the first phase of germination the same quantity of asparagine is formed in the light as in the dark, whilst at a later stage the asparagine disappears in plants germinating in the light, but persists in the etiolated plant. This last observation is explained by admitting that asparagine becomes transformed into proteids by means of the carbohydrates produced by assimilation, and when these are used up to sustain respiration, the asparagine consequently accumulates. The seeds of peas, haricots, lupins, and beans do not contain asparagine. In the seeds of yellow lupins, grown in water in the light, the author found tyrosine, which is absent in seeds grown in the ordinary manner.

J. M. H. M.

Determination of Undecomposed Fat in Mixtures of Fatty Acids. By O. HAUSAMANN (*Dingl. polyt. J.*, **240**, 62—65).—The author mentions that Nitsche's method depending on the insolubility of the neutral fats in alcohol, is not trustworthy, as the neutral fats are not altogether insoluble, even in pure alcohol; moreover the method occupies a long time. The latter objection applies also to the glycerol method, hence it is best to determine the fatty acid in the fatty masses by titration. By adding caustic alkali to an alcoholic solution of fatty acid and neutral fat, drop by drop, the free fatty acid only becomes fixed, the neutral fat remaining unaltered; but if an excess of alkali is added at once, the neutral fat is decomposed, and is converted into a soap, together with the fatty acid. This method can be applied to manifold determinations, *e.g.*, for investigating the progress of the decomposition in the autoclaves, in order to determine by intermittent titrations the quantity of fatty acid which is formed.

D. B.

Composition of Milk from the same Cow on Consecutive Days. By C. v. BORRIES (*Bied. Centr.*, 1881, 63).—The analyses show that very great variation exists in the daily composition of cow's milk.

E. W. P.

Technical Chemistry.

Photochemistry of Silver Bromide. By J. M. EDER (*Chem. Centr.*, 1880, 748—752, and 761—768).—The experiments referred to below were all made with emulsions of the haloïd silver salts.
(a.) *Silver bromide disseminated through an indifferent substance, such*

as collodion pyroxylene. Silver bromide, prepared with an excess of silver nitrate, and in thin layers, is white by reflected light, and permits the penetration of more light from the violet than from the red end of the spectrum; it is much more sensitive than when prepared with excess of potassium bromide, and is also far more easily reducible by chemical developers. This action probably depends on the presence of traces of silver nitrate. Bromide of silver, prepared with excess of potassium bromide, is yellow by reflected light. By increasing the excess of soluble bromide, the sensitiveness is rapidly diminished, whereas the presence of soluble chlorides has no effect in this respect.

(b.) *Silver bromide, disseminated through an easily oxidisable organic substance*, such as gelatin or gum, which favours the reduction of the silver salt by light. Silver bromide, prepared with excess of nitrate, is but little more sensitive than when prepared with excess of bromide, although it forms a more intense picture. Large excess of silver nitrate induces a reduction of the bromide, even if light is excluded. Bromide of silver suspended in gelatin, with a slight excess of soluble bromide, is from 4 to 6 times more sensitive than when disseminated through indifferent collodion with excess of nitrate, and 20 to 40 times more sensitive than a bromide of silver emulsion with excess of soluble bromide prepared with collodion. Large excess of soluble bromide is very objectionable. A day's digestion of the aqueous silver bromide gelatin emulsion at 30–50° C., greatly increases its sensitiveness, and causes it to assume a green colour by reflected light, and no longer permits the penetration of red rays, but allows the passage of a large proportion of blue rays. After several days' digestion, the emulsion becomes much more sensitive than any other known body. These results refer more especially to preparations made with an excess of soluble bromide. After very long digestion (8–14 days) it is blackened by developers, even though light has been excluded. A moderate temperature (30–60°, according to circumstances) for digestion in the preparation of the emulsion, favours its sensitiveness, whilst the presence of too much soluble bromide has the opposite effect. The bromide should not be increased beyond 24 parts of KBr to 30 parts of AgNO₃. Free chlorine, bromine, iodine, and nitrous acid destroy the sensitiveness if allowed to act before exposure to light, and after exposure prevent the development of the latent picture. Halogen acids, sulphuric acid, and organic substances, such as acetic acid, also have a deleterious effect, although less so than oxidising agents. Perchlorides entirely destroy the latent picture; monochlorides and monobromides delay the photochemical action; whilst alkalis, and more especially ammonia, accelerate it considerably, owing probably to its increasing the solubility of the silver salts. The author recommends the following process for preparing a plate of greater sensitiveness than any other:—A gelatin emulsion is made by digesting at 32–46° for from four to seven days, whereby the silver bromide is obtained in a very finely-divided granular condition. The emulsion is then allowed to cool to 37°, and 1½ to 2 per cent. ammonia added, and the whole digested for 1½ to 2 hours at this temperature; the emulsion is then allowed to solidify, and after washing, is ready for use.

Organic bodies which absorb bromine (as gelatin, tannin, &c.) act as sensitisers in presence of soluble bromide, but not in presence of excess of silver nitrate. In all cases, the direct development of the silver bromide by an oxidisable body greatly favours the sensitiveness of the plate. Temperature differences of 5—25° appear to have no influence. Damp plates are less sensitive than dry plates. The stronger the reducing action and the more concentrated the developer, the shorter the time required for exposure; warming of the developer by 5° or 10° has also the same effect. Electrochemical actions appear to play an important part in the development of the latent picture. The author considers that the photochemical decomposition of silver bromide is not a special process, but is the result of a partial loss of bromine, which is also producible by other means. It has long been known that silver iodide, prepared with an excess of soluble iodide, is scarcely sensitive to light, and prepared with excess of nitrate, is less sensitive than the analogous bromide of silver, although iodide of silver is much more sensitive towards developers than either the chloride or bromide. Mixtures of bromide and iodide are less sensitive than the pure bromide, and mixtures of bromide and chloride have no special advantage. T. C.

Novelties in the Soda Industry. (*Dingl. polyt. J.*, 239, 392—401).—G. Lunge, in continuation of former communications (this vol., 193), gives a method for the estimation of sulphur in pyrites, which avoids the sources of error incidental to Fresenius's process, namely, the solubility of the barium sulphate in hydrochloric acid and ferric chloride, and the precipitation of ferric oxide along with the barium sulphate. As soon as the clear solution boils, it is removed from the source of heat, precipitated with a boiling solution of barium chloride, allowed to remain for 15—20 minutes until clear, and washed first by decantation with boiling water, and then on to the filter in the usual way. The solution should on no account be heated after the barium chloride has been added, as otherwise iron is precipitated.

Powell proposes to prepare calcium sulphate by passing sulphurous anhydride (and air?) over powdered calcium oxide, hydrate, or carbonate. Pohl prepares sodium sulphate by passing sulphurous anhydride and air into a boiling solution of sodium chloride.

Rendering Soda-lye Caustic.—Jurisch states that, on the average, 1,000 kilos. of 70 per cent. caustic soda contains 670 kilos. Na_2O as sodium hydrate, and 30 kilos. Na_2O as carbonate. To render this 670 kilos. Na_2O caustic if it existed as carbonate, would require 605·16 kilos. CaO ; in practice, however, it is found to require 678·8 kilos. CaO , or 738 kilos. of good lime (92 per cent. CaO). As, however, soda ash and red liquors both contain caustic soda ready formed, proportionally less lime is required. The author also notices the loss of sodium compounds remaining in the lime sludge (comp. this vol., p. 508). In order to avoid this, Parnell employs a lye of 1·16 to 1·18 sp. gr., and heats at 140° to 145° under pressure, when little or none of the lime compound containing sodium is formed. A short description is given of the special form of apparatus he employs. The lye obtained in this way is evaporated until it boils at 121°;

sufficient sodium nitrate is then added to entirely decompose the sulphides, and the evaporation continued until the temperature rises to 149° . It is then allowed to cool, and the salts which separate are removed. The clear lye is then drawn off and again evaporated. Experimental trials have been made of rendering the liquors of 1.13 to 1.16 sp. gr. caustic by long heating with lime in open vessels, air and steam being blown in.

In analysing the lime sludge, Parnell recommends the following process for determining the CaCO_3 , CaO , and Na_2O :—

(1.) 10 grams are titrated with normal nitric acid (A c.c. suppose), after the sulphides, &c., have been oxidised by hydrogen peroxide.

(2.) 10 grams are decomposed with ammonium chloride and sufficient water to keep in solution all the ammonia liberated by the free lime and soda, make up to 500 c.c., and titrate 250 c.c. of the clear solution with normal nitric acid (B c.c. for the 10 grams suppose).

(3.) 10 grams are repeatedly evaporated to dryness with ammonium carbonate to convert the free lime into carbonate; on extracting with water, the sodium carbonate is dissolved and estimated by standard acid (C c.c. suppose). Instead of using ammonium carbonate, carbonic anhydride may be passed into the solution. In calculating the amount of the three chief ingredients, the following formulæ may be used :—

$$\text{CaCO}_3 = (\text{A} - \text{B}) \text{ c.c.}, \text{CaO} = (\text{B} - \text{C}) \text{ c.c.}, \text{and } \text{Na}_2\text{O} = \text{C c.c.}$$

J. Wells and also J. Menzies propose to render alkalis caustic by treating the carbonates with lime under pressure, but without the application of heat.

C. E. G.

Oxidation of Soda-liquors. By K. W. JURISCH (*Dingl. polyt. J.*, **240**, 55—61).—In order to occasion a saving in saltpetre in the manufacture of caustic soda, the oxygen of the air has been used for the last 25 years to oxidise the sodium sulphide present in the liquors. Although the oxidation of the sulphide only advances sufficiently to form sodium dithionate, the process is very economical, as the oxidation may be completed with one half the usual quantity of saltpetre.

Since 1878 the “red liquors” have been oxidised in vertical cylinders, instead of being treated in flat pans, which always gave rise to imperfect oxidation. The oxidation cylinders are 4 meters high and 2.3 meters in diameter. A pipe 15 cm. thick is fixed in the centre of the cylinder, the upper end of which carries a Körting’s injector, whilst the lower end, about 30 cm. from the bottom of the cylinder, is connected with a system of perforated branch-pipes, the holes 5 mm. wide, looking downwards. The charge amounts to about 7,000 litres of “red liquors,” of 50 — 60° Twaddle per cylinder. 7,000 litres at 200 grams (per litre) total Na_2O , contain 1,400 kilos. Na_2O . One ton 70 per cent. caustic soda contains 700 kilos. Na_2O ; hence each charge would yield 2 tons caustic soda. However, as only three-fourths of the alkali present in the liquors is utilised in the formation of caustic soda, the other fourth being separated in the form of salts, each charge produces 1.5 tons of caustic soda. The cost of fuel in oxidising

enough liquors to produce 1 ton caustic soda is estimated at 4.65 marks, taking the price of coal at 6 marks per ton.

Pauli's method is said to be still more economical. It is proposed to use 1 gram MnCl_2 for 1 litre soda liquors, but it has been found more advantageous to utilise Weldon-mud of the same constitution as used for the preparation of chlorine. The oxidation of the sodium sulphide is materially facilitated by the presence of the manganese dioxide, which is reduced. The MnO may become oxidised immediately to Mn_2O_3 or MnO_2 , and thus act as a transferer of atmospheric oxygen to the sodium sulphide. This process is said to go on until all the sodium sulphide has been oxidised. D. B.

New Methods for the Desulphurisation of Alkaline Solutions. By SCHEURER-KESTNER (*Compt. rend.*, 92, 878—881).—The sulphides in alkaline liquids are usually oxidised by blowing a stream of air through the liquid. The operation may be facilitated and rendered much more rapid by adding manganese dioxide, in the form of paste, in the proportion of 20 kilos. of the oxide to about 1,200 kilos. of sodium salt. Under these conditions the oxidation takes place in little more than half the time required when a stream of air is simply blown through the liquid. The manganese dioxide oxidises the alkaline sulphide, and the reduced oxide is again oxidised by the oxygen of the air blown in. When using the old method, oxidation of the sulphide ceases with the formation of thiosulphate; when manganese is added, the thiosulphate is partially, although never entirely, converted into sulphate. If it is necessary to completely oxidise all sulphur compounds, the electrolytic method of Merle and Co. may be employed. For this method a voltaic current is more economical than a current from a dynamo-electric machine. When it is not necessary to carry the oxidation further than the formation of thiosulphate, oxidation by means of a current of air, with addition of manganese, is cheaper than the electrolytic method. C. H. B.

Phosphorite from the South of France. By L. L'HOTE (*Bied. Centr.*, 1881, 14).—Phosphorite from the south of France contains 70 per cent. of tricalcium phosphate and 12 of carbonate. For the preparation of precipitated phosphate from this mineral, and indeed from others poorer in phosphate, it is recommended to heat the mineral to a dull red in a current of steam, when the carbonate is decomposed, and the resulting mass is friable. The powder obtained is then treated with very dilute acid, when the phosphate sinks to the bottom of the vessels, remaining undissolved. Thus a poor phosphate may be concentrated by removal of the other forms of calcium.

E. W. P.

Malleable Cast-iron. By L. FORQUIGNON (*Compt. rend.*, 91, 817—819).—Since the discovery of malleable cast-iron by Réaumur in 1772, very little work has been done in connection with the chemistry of this substance. The calorimetric experiments of Troost and Hautefeuille have shown that white iron is produced with absorption of heat: its carbon is wholly in combination with the iron, and at a temperature below its melting point it is permanently

softened, whilst a deposition of carbon in the form of graphite takes place throughout its whole mass. This graphite is absolutely amorphous, even when magnified 400 diameters; it appears to be a new variety of carbon, if certain special characteristics of its "graphitic acid" may warrant any one in making such an assertion.

The foregoing reaction takes place only when the iron is heated in an inert medium, in charcoal, for example; when the metal is in contact with a substance capable of burning or absorbing its carbon, a secondary action results, the free carbon being eliminated from the exterior layers, the equilibrium set up by the heating becomes slowly modified, a portion of the graphite from the centre of the bar re-enters into combination, travels towards the exterior, and disappears; this is replaced in its turn by another portion, and so on until the iron is reduced to a minimum of carburization.

A small proportion of manganese, less than a five-thousandth part, hinders the softening of the iron, and this property absolutely ceases to be appreciable when the quantity of manganese reaches 2 per cent. The iron may still continue to lose carbon by oxidation, and indeed does so as readily as when there is no manganese present, but the latter prevents entirely the production of graphite, and retains the carbon in combination throughout the metallic mass. Silicon can, however, to a certain extent saturate the manganese, and thus set the graphite at liberty, and allow softening to take place.

The following facts have been made out:—

- (1.) That a true malleable cast-iron always contains graphite.
- (2.) A cast-iron can lose carbon, and nevertheless remain brittle, if no graphite has been formed, or if the quantity of graphite existing before heating is not increased.
- (3.) A cast-iron can become malleable and soft without sensibly losing any of its carbon, as, for instance, when it is re-heated in contact with charcoal.

Hydrogen gas at 900° rapidly decarburises white iron, whilst a portion of the hydrogen is occluded by the metal, and remains, according to the author, in combination with the residuary carbon. Nitrogen also is said to exert a similar and equally energetic action.

Malleable cast-iron appears to be intermediate between steel and grey iron. It differs from the latter by the special nature of its *amorphous graphite*, and by its greater tenacity; and from steel by its large percentage of carbon, and by its feeble wire-drawing power.

J. W.

Removal of Earthy Matters from Poor Lead Ores by Means of an Air-blast. By M. DELESSE (*Compt. rend.*, 91, 791—793).—In mining districts where there is a deficient supply of water, the process of washing ores in order to remove the earthy portions cannot be well adopted, hence a method was devised in which a blast of air applied in a suitable manner was made to do the work which is usually effected by water. The process has been carried out with tolerable success in connection with the poor lead ores of Génolhac. Without entering into details respecting the construction of the apparatus, it is sufficient to say that a strong current of air is forced through successive layers of metallic webbing, of which the dimensions

are respectively 4 mm., $\frac{1}{2}$ mm., and $\frac{1}{10}$ mm. The air thus perfectly sub-divided passes directly into a rectangular box, at one extremity of which the material in coarse powder is introduced in a regular manner by means of a hopper. As soon as it meets the air-blast, it is blown in the direction of the further end of the box, but the poorer portions, that is, those containing less lead, are suspended and carried away to a considerable distance by the blast, whilst the heavier and richer portions of the ore fall almost perpendicularly; by means of a series of receptacles, the ore can be thus separated into various qualities. The material must not be too finely ground, or the apparatus does not work in a satisfactory manner. As an example of the extent to which the percentage can be raised by the use of the blast, an ore containing only 9 per cent. of lead was raised to 14 per cent. after one operation, and by repassing the enriched sample through the apparatus a second time, it was raised to 27 per cent. It is noticeable, however, that the proportion of silver steadily diminishes at each operation; thus in the examples given above, the proportion of silver in the ore after treatment was 55 grams per quintal of lead; whilst it reached as high as 81 grams in the rough ore. An attempt was made to work with the air-blast the galena of Génolhac, which has a quartzose and dolomitic gangue, but unsatisfactory results only were obtained. J. W.

Novelties in Metallurgy. (*Dingl. polyt. J.*, 240, 148—155).—Mosler describes the copper mining at Lake Superior. The analysis of the refined metal shows that it is very pure.

Cu.	S.	Ag.	Fe.	O.
99.961	0.002	0.028	0.007	0.002

In order to obtain compact and malleable copper-castings, Walker proposes to treat the melted copper with 1 per cent. cryolite, 0.25 per cent. acetate of lead, and 1 per cent. borax, and to pour the copper into moulds after 10 to 15 minutes.

In refining copper, Hering forces air through the melted mass after the withdrawal of the first slag, until a sample taken from the fused metal shows that iron is absent. If arsenic or antimony is present, chlorine is first passed through the bath, and when a sample on testing shows the absence of these impurities, air is again introduced into the mass. The bath is then freed from dross and the copper reduced by means of poling, *i.e.*, introduction of carbonic oxide. The dross is again removed and the copper exposed to the toughening process. The bath is covered with charcoal, and a current of carbonic oxide and phosphorus vapour passed through until the copper has attained its full degree of toughness, whence it is at once ladled out into moulds.

Schnabel's process of desilverising raw lead by zinc depends on the decomposition of the alloy by means of steam into a metallic and an oxidised part; the latter is freed from zinc by means of carbonate of ammonium, and the mixture of argentiferous lead and oxide of lead is desilverised by cupellation of the metallic part.

Langer describes the preparation of copper, silver, and mercury at the "Stefans-foundry in the Zips" on a large scale.

Scheneck has made a series of experiments on the Schmöllnitz cementation-waters. Hitherto the quantity of iron used was 389 kilos. for every 100 kilos. cementation copper. It was found that by passing the waters over a mixture of iron and coke, 262 kilos. of iron were dissolved for every 100 kilos. of precipitated copper.

In order to obtain silver and gold from ores containing sulphur, arsenic, and antimony, de Vaureal proposes to heat the finely pulverised ore to redness in a retort, and to introduce hydrogen gas simultaneously. Thus the sulphur is volatilised as sulphuretted hydrogen and the arsenic removed by sublimation. The residue is ignited in the air, treated with sulphuric acid to dissolve the oxide of copper formed, then with concentrated hydrochloric acid to dissolve the oxides of antimony. The chloride of silver in the residue is reduced with milk of lime and a small quantity of molasses, and fused with litharge and charcoal.

Dietzsch (*Berg- und Hüttenmänn. Zeit.*, 1888, 33 and 57) describes the occurrence of gold in the limestone rocks of Persia; Williger (*ibid.*, 1881, 65) gives some data as to the presence of gold in Silesia; and Dietzsch (*ibid.*, 1881, 13) discusses the preparation of gold from sulphuretted ores. A minute account of the geological occurrence of gold and platinum in Russia appeared in *Engineering*, 1881, 31, 163.

It is mentioned that Plattner's process of separating gold from the substances with which it is mechanically associated by means of chlorine gas is less economical than amalgamation.

Van Riemsdijk (*Berg- und Hüttenmänn. Zeit.*, 1880, 247; 1881, 2) discusses the flashing of gold, which he attributes to superfusion.

D. B.

Wilkinson's Process of Making Illuminating Gas from Wood. By C. A. DOREMUS (*Chem. News*, 43, 57).—By heating Virginia pine in "through retorts," and pushing the resulting charcoal, after the first charge, back in the retort, and allowing the gas made from the second charge to traverse this bed of red-hot coal, the following product is obtained:—

H.	CH ₄ .	CO.	CO ₂ .	N.	O.	NH ₃ .	H ₂ S.
5.40	44.16	33.75	10.50	6.00	0.25	none	

Illuminants none. The above is the composition of the crude gas after cooling, 3,300 lbs. pine yielding 53,832 cubic feet. To give the wood-gas the requisite illuminating power, it is carburetted according to the "binary" process adopted at Buffalo in 1872, which alters its composition as follows:—

H	CH ₄ .	CO.	CO ₂ .	N.	O.	NH ₃ .	H ₂ S.	Illu- minants.
57.75		11.25	1.00	15.00	0.75	none		15.25

21 volumes of wood-, 37.4 of coal-, and 41.6 of naphtha-gas make 100 of commercial wood-gas. 4.5 gallons naphtha are required for 1,000 cubic feet of gas of a candle power of 26.53.

D. B.

Removal of Carbon Bisulphide from Commercial Benzene.

By B. NICKELS (*Chem. News*, **43**, 148—149).—The author applies Macagno's method for the estimation of carbon bisulphide (this vol., 308) to its removal from benzene.

200 c.c. benzene are treated with 20 c.c. of a hot saturated solution of potash in absolute alcohol, methylated or otherwise, and frequently shaken during two hours. The benzene is then separated from the potassium ethyl dithiocarbonate which is formed, washed free from alcohol with water, and finally dried over plaster of Paris. The sp. gr. and refractive index of the commercial benzene thus purified will indicate its composition.

The author suggests the application of this method to the removal of carbon bisulphide from benzene on the large scale.

L. T. O'S.

Grape-sugar from Starch. By F. ALLIEN (*Landw. Versuchs.-Stat.*,

26, 312—318).—The author found in four samples of commercial starch-sugar only 60 to 66.4 per cent. of grape-sugar. He found, on converting starch into sugar by digestion with dilute sulphuric acid, that the yield of sugar increased up to a certain point with the concentration of the acid and the time employed. Experiments were made by heating the solutions at 100°, and, under pressure, at 108° and 114° respectively. Acid of 1 per cent. strength at 108° converts 90 per cent. of starch into sugar in four hours, or, at 114°, in three hours. This process yields a product with about one-third the impurity of ordinary commercial starch-sugar. By washing with alcohol, or by pressing, the greater part of this dextrin syrup can be easily removed.

J. T.

Hurtful Action of Potato-sugar. By R. C. KEDZIE and others

(*Bied. Centr.*, 1881, 44—47).—Kedzie shows that many sugar syrups made in America have a hurtful action on the human system, and has found in a gallon of syrup, of free sulphuric acid, 9.19 grams, of ferrous sulphate, 1.62 grams, and of lime, 46.91 grams. Potato-sugar employed for the manufacture and improvement of wine and beer often contains, according to Nessler and Barth, a considerable quantity of an unfermentable substance; this produces illness in those persons who drink of the spirit prepared from such sugar. The same effects, according to Schmitz, are produced by the unfermentable compounds present in commercial grape-sugar.

E. W. P.

New Fermentation of Beetroot-molasses. By A. NEALE,

M. MÄRCKER, and H. BRIEM (*Bied. Centr.*, 1881, 48—57).—It frequently happens that beetroot-molasses resist the action of the ferments. When alkaline, they will not ferment at all; but when they are acidified with sulphuric acid, fermentation proceeds, although very slowly and incompletely. Such molasses are found to contain, besides the usual substances, butyric, caproic, and other organic acids, nitrates and nitrites. Experiments show that this resistance to fermentation is due to the nitrites and free acids (except acetic), especially caproic acid. When such molasses are worked, it is advisable to add chalk,

which, by removing the organic acids, renders the condition of the molasses normal. E. W. P.

Creaming of Milk in Earthen Pans. By M. SCHRODT (*Bied. Centr.*, 1880, 897—899).—This is a report of a series of experiments on the amount of cream obtainable from the same milk when set in wooden, earthen, and tin-ware vessels. The time was 24 and 36 hours; and in both cases the results were greatly in favour of the tinned ware over the wooden vessels; the earthen approached them closely, but both were far superior to the wood. The metal is more strongly recommended, as the liability to breakage is so much less. Wood is considered unsuitable when the other materials are available.

J. F.

Composition of Cream and Skim-milk from De Laval's Centrifugal Separator. By A. VOELCKER (*Bied. Centr.*, 1880, 896).—The author had occasion to examine samples from this apparatus at the Kilburn Show, and reports the composition of fresh and skimmed samples:—

	Fresh.	Skimmed.
Water.....	87.72	90.71
Fat.....	3.45	0.22
Casein.....	3.12	3.31
Milk-sugar.....	5.11	5.12
Mineral matter.....	0.60	0.64
	<hr/> 100.00	<hr/> 100.00

Two other samples skimmed by this method showed 0.46 per cent. and 0.31 per cent. fat.

Milk skimmed in the ordinary manner showed, in the skim-milk, 0.75 per cent., and the cream 25 per cent. of fat.

Cream obtained by means of the De Laval's separator had the following composition:—

Water.....	66.12
Fat.....	27.69
Casein.....	2.69
Milk-sugar.....	3.03
Inorganic matter.....	0.47
	<hr/> 100.00

The results are considered very favourable for Laval's separator.

J. F.

American Preserved Meats. By A. MAYER (*Bied. Centr.*, 1881, 57).—Analyses of three sorts of tinned meats are given. All three contained metal; in one case as much as 0.09 gram was found, partly in the free state, and partly oxidised. E. W. P.

Inflammability of Vegetable Substances with Nitric Acid. By R. HANS (*Ber.*, 14, 597—599).—The author has found that when

dry hay, straw, tow, or blotting-paper is closely packed in small chests, soaked with nitric acid, and a lid placed on until the evolution of nitrous fumes is conspicuous, then, if the lid is removed, the whole of the contents of the chest glow, and, with a breath of air, burst into flame. A similar result has also been obtained by Kraut (*Ber.*, 14, 301).

A goods waggon belonging to the Baden Railway was burnt from this cause. V. H. V.

Action of Oils on Metals. By W. H. WATSON (*Chem. News*, 42, 190).—With regard to the action of various oils on copper, the author arrived at the following conclusions:—

1. That of the whole of the oils used, the samples of paraffin and castor oils had the least action, and that sperm and seal oils were next in order.

2. That the appearances of the paraffin and the copper were not changed after 77 days' exposure.

3. That different oils produce with copper compounds varying in colour, or in depth of colour, and consequently rendering comparative determinations of their action on that metal, from mere observations of their appearances, impossible.

The author found that there is no relation between the action of an oil on copper and the action of that oil on iron; that, in fact, in several cases those oils which act strongly on iron, act but slightly on copper, and *vice versa*. The actual extent of action of the same oil (with the exception of paraffin) is of course greater on copper than iron. The following oils were experimented with, and observations were made after 24 days' exposure:—

	Grains iron.	Grains copper.
Neatsfoot oil (English)	0·0875	0·1100
Colza „	0·0800	0·0170
Sperm „	0·0460	0·0030
Lard „	0·0250	—
Olive „	0·0062	0·2200
Linseed „	0·0050	0·3000
Seal „	0·0050	0·0485
Castor „	0·0048	—
Paraffin „	0·0045	0·0015
Almond „	0·0040	0·1030
Special lubricating oil	0·0018	—

D. B.

General and Physical Chemistry.

Sensitiveness of Silver Bromide Dry Plates for Different Portions of the Solar Spectrum. By H. W. VOGEL (*Ber.*, **14**, 1024—1028).—After referring to his previous researches on the action of light on the haloïd silver salts (this Journal, 1874, 217, 424, and 736), the author points out that silver bromide gelatin plates are most sensitive to pale blue rays (450 wave-lengths). The sensitiveness gradually diminishes in the direction of the violet and rapidly in the direction of the red rays; whereas silver bromide collodion plates are most sensitive to indigo rays (430 wave-lengths), the action decreasing rapidly towards the green, and gradually towards the ultra-violet rays. The difference in the sensibility of collodion and gelatin plates is due to the fact that they contain two different modifications of silver bromide.

Collodion-gelatin plates, prepared by mixing a solution of gelatin containing finely-divided silver bromide in glacial acetic acid with a solution of pyroxylin in glacial acetic acid and alcohol, are as sensitive as gelatin plates. They resemble the gelatin plates in their maximum of sensibility and in their behaviour to the violet end of the spectrum, but are much more sensitive to the rays of lesser refrangibility. The conversion of a negative into a positive image, by over exposure to strong light, takes place much less readily with collodion-gelatin than with gelatin plates.

W. C. W.

Action of the Air in Rendering the Flame of the Bunsen Lamp Non-luminous. By K. HEUMANN (*Ber.*, **14**, 1250—1253).—In reply to Blochmann's remarks (*Annalen*, **207**, 167), the author points out that the non-luminosity of the flame of a Bunsen's burner to which air is admitted is due to several different causes, some of which act in opposite directions; *e.g.*, the dilution of the gas with the inert nitrogen of the air tends to diminish the luminosity of the flame by lowering its temperature, but this action is not directly perceptible, since it is more than counterbalanced by the increase of temperature due to the admission of oxygen. The luminosity of a hydrocarbon flame is decreased by anything which hinders the separation of free carbon.

W. C. W.

Discontinuous Phosphorescent Spectra in High Vacua. By W. CROOKES (*Chem. News*, **43**, 237—239).—The author some time ago drew attention to the fact that many substances, when submitted in high vacua to the molecular discharge by means of an induction coil, emitted phosphorescent light, the phosphorescent sulphides, the diamond, the ruby, and various other forms of alumina, crystalline and amorphous, being mentioned. Pure alumina, chemically prepared, has very strong phosphorescence; alumina, in the form of ruby, glows with a full rich red colour, and the emitted light, when examined with the spectroscope, is seen to be discontinuous. There is a faint con-

tinuous spectrum ending in the red, somewhere near the B line, then a black space, and next an intensely brilliant and sharp red line, to which nearly the whole of the intensity of the coloured glow is due. This coincidence is of considerable interest, as it shows a relation between the action of molecular impact and of sunlight in producing luminosity. The phosphorescence induced in a crystal of ruby by the molecular discharge is not superficial, but the light comes from the interior of the crystal, and is profoundly modified according as its direction of vibration coincides or makes an angle with the axis of the crystal, being quenched in certain directions by a Nicol prism. Sunlight falling on the ruby crystal produces the same optical phenomena. The crimson glow of alumina remains visible some time after the current ceases to pass. When the residual glow has ceased, it can be revived by heating slightly with a spirit-lamp.

After long experimenting with chemically pure alumina precipitated from the sulphate, a curious phenomenon takes place. When sealed up in the vacuum two years ago, it was snow-white, but after being frequently submitted to the molecular discharge, it gradually assumes a pink tinge, and on examination in sunlight, a trace of the alumina line can be detected. The repeated molecular excitation is slowly causing the amorphous powder to assume a crystalline form. The following experiment was made:—Two earthen crucibles were tightly packed, the one with sulphate of alumina, the other with the acetate. They were then exposed, side by side, to the most intense heat of a wind-furnace—a heat of nearly the melting point of platinum. The resulting aluminas were then tested in the molecular stream; the sulphate gave a crimson glow and spectrum line, the acetate gave no red glow or line, but a pale-green phosphorescence. Besides the ruby, other native forms of crystallised alumina phosphoresce; corundum glows with a pink colour; sapphire gives a red and green glow; the mineral spodumene (aluminium and lithium silicate) gives a brilliant rich golden-yellow colour, but shows no spectrum line, only a strong concentration of light in the orange and yellow.

The author in the next place investigated if the other earths would show phosphorescent properties similar to those of alumina, and especially if any of them would give a discontinuous spectrum. Glucina phosphoresces with a bright blue colour, but no lines can be detected in the spectrum, only a concentration of light in the blue. Phenakite (aluminate of glucinum) behaves like glucina, but shows a residual glow after the current is turned off. Thorina has very little, if any, phosphorescence. However, on putting it in a tube furnished with well insulated poles, whose ends are about a millimeter apart in the centre, and heating strongly during exhaustion, the earth on cooling absorbs the residual gas with such avidity that the tube becomes non-conducting, the spark preferring to pass several inches in air rather than strike across the space of a millimeter separating the two poles. It is probable that this strong attraction for gas is connected with the great density of the earth thorina (sp. gr. 9.4). Zirconia gives a very brilliant phosphorescence of pale bluish-green colour. No lines are seen in the spectrum. Lanthana shows no phosphorescence. After it has been heated for some time before the blowpipe, it phosphoresces

of a rich brown. Didymia has scarcely any phosphorescence. Yttria shows a dull greenish light, giving a continuous spectrum. Erbium phosphoresces with a yellowish colour, and gives a continuous spectrum. Titanic acid phosphoresces dark brown, with gold spots in places. Stannic, chromic, ferric, and ceric oxides do not appreciably phosphoresce. Magnesia phosphoresces with a pink opalescent colour, and shows no spectrum lines. Baryta (anhydrous) scarcely phosphoresces at all. The hydrate shines with a bright orange-yellow light, but shows no discontinuity of spectrum, only a concentration in the yellow-orange. Strontia phosphoresces with a beautiful deep-blue colour, without any lines or bands. Lime phosphoresces of a bright orange-yellow colour, changing to opal-blue in patches, where the molecular discharge raises the temperature. On stopping the discharge, there is a decided residual glow. No lines are seen in the spectrum of the light. Calcium carbonate shows a strong phosphorescence, which begins to appear at a comparatively low exhaustion (5 mm.). The interior of the crystals shines of a bright straw colour, and the ordinary and extraordinary rays are luminous with oppositely polarised light. Calcite shows the residual glow longer than any substance experimented with. Calcium phosphate gives an orange-yellow phosphorescence and a continuous spectrum. Potash phosphoresces faintly of a blue colour without lines. Soda phosphoresces faintly yellow, and gives the yellow line in the spectrum. Lithium carbonate gives a faint red phosphorescence, showing the red, orange, and blue lithium lines in the spectroscopic. The diamond phosphoresces with great brilliancy. In this respect perfectly clear and colourless stones "of the first water" are not the most striking, and they generally glow of a blue colour. Diamonds, which in sunlight have a slight fluorescence, disappearing when yellow glass is interposed, generally phosphoresce more strongly than others, and the emitted light is of a pale yellowish-green colour. Diamonds which phosphoresce red generally show the yellow sodium line superposed on a continuous spectrum.

With regard to the degree of exhaustion at which various substances begin to phosphoresce, it is mentioned that the majority of bodies do not phosphoresce until they are well within the negative dark space.

During the analysis of some minerals containing the rarer earths experimented on, certain anomalies have been met with, which seem to indicate the possible presence of other unknown elements awaiting detection.

D. B.

Galvanic Polarisation. By F. EXNER (*Wien. Akad. Ber.*, 82 [ii], 1091—1100).—This is in answer to Beetz's papers (this Journal, 38, 837).—The author is of opinion that a given metal in a given gas does not produce a constant quantity of polarisation; but that this quantity, for example, in the case of platinum in hydrogen, depends essentially on the way the hydrogen in the voltameter is utilised; for if the second electrode be either copper in a solution of copper sulphate or silver in a solution of silver nitrate, then the polarisation current is due either to the reduction of the copper or of the silver; and as these reductions are not thermally equal, they will each yield a different electromotive force of polarisation. From this he draws the

conclusion, that the estimation of the polarisation of only one electrode, as a constant, is valueless. Beetz objects to this, and supported his objection by the experiment with the three separate cells, *Z*, *A*, and *B*, which were connected together by a tube of acidulated water (*loc. cit.*). The current from a primary circuit going through a voltameter had its electrodes in *A* and *B*; *Z* contained an amalgamated zinc plate, and was in connection with *A*. The circuit being closed and the ions disengaged, the polarisation of *A* was measured, by connecting it with the earth, and *Z* with an electrometer. *A* contained platinum in dilute sulphuric acid; *B* was first platinum in sulphuric acid, then zinc in zinc sulphate, copper in copper sulphate, and silver in silver nitrate. The author, however, shows that the method of proof, and not the thesis, is at fault; for if the middle cell *A* be connected with the earth, and the cell *Z* with an electrometer, then the polarised platinum plate is always opposed to the same electrode, and therefore the force is always the same, whatever *B* contains. The metal and liquid ought to have been changed in *Z*, and not, as Beetz did, in *B*.

The author states further, that the positive pole of an element, if it is not chemically altered, takes no part in the production of electricity. His experiments agree with this statement; Beetz's do not. He accounts for this from the fact that he used water free from oxygen, which Beetz did not; therefore, in the case of the elements, Zn—Ag; Zn—Cu, the loss of electromotive force was due to the oxidation of the positive poles; whilst in the case of the Na—Zn element, it was due to the fact that there was one current from the sodium in one direction, and another caused by the decomposition of the water and the simultaneous oxidation of the zinc, in the opposite direction; this being the case, the force of the element Na—Pt = 1.33, less the force of the element, Zn—Pt = .73, difference = .60, should equal the force of Na—Zn; Beetz found .68. Beetz objects to this explanation, because, after allowing a Na—Zn element, in which the two plates were put in separate vessels connected by a tube filled with acidulated water, to work for 17 hours, he found zinc sulphate in the liquid round the zinc plate, but none in that round the Zn—Na plate; he infers that "even zinc, when negative in the circuit, is not attacked by dilute sulphuric acid." The author, however, explains it this way: the current from the sodium being the stronger, decomposes the zinc sulphate as soon as it is formed, and deduces further that this Na—Zn element is, in fact, two elements working one against the other. He refers to another point, viz., the relation of the electromotive force of the primary current to that of the polarisation current (this *Journal*, 36, 578), about which Beetz quotes contradictory statements.

D. A. L.

Elasticity and Electric Conductivity of Carbon. By W. BEETZ (*Ann. Phys. Chem.* [2], 12, 65—75).—The modulus of elasticity of the coke used for the electric light is deduced from the note emitted when a piece is thrown into acoustical vibration. The experiments on the electric conductivity show an irregular decrease in the resistance with the rise of temperature at first, and afterwards an increase. The author explains the irregularity by attributing to the

coke a structure similar to that of certain metallic oxides (*e.g.*, *pyrolusite*).
R. R.

Thermic Theory of Galvanism. By J. L. HOORWEG (*Ann. Phys. Chem.* [2], 12, 75—90).—In this paper the author concludes the exposition of his theory as applied in detail to the phenomena of electricity, and sums up the whole in the following propositions:—

1. Every development of electricity is a consequence of the disturbed motion of heat in the contact of two heterogeneous bodies.

2. Electricity is propagated from one point to another in two different ways, namely, by conduction and by dielectric action.

3. Bodies may be divided into dielectric and adielectric. The conductivity of the former class increases with the temperature; that of the latter decreases.

4. An electrolyte is a decomposable dielectric.

5. In every closed circuit of which at least one member is a dielectric, the sum of the differences of potential is not zero. The least variation of potential adjusts itself in the circuit, but is continually re-established by the heat: hence a galvanic current is produced, the direction of which is determined by the sign of the aforesaid sum.

6. The galvanic current subsists at the expense of heat at some of the points of contact, and causes the development of heat at others. It continues if sufficient heat is supplied from without (thermo-current) or from within (voltaic current); otherwise it disappears with a rapidity determined by the resistance of the circuit.

7. The electrolytes in the circuit are always decomposed, and this usually produces new differences of potential, which together diminish the above-mentioned sum, and may even reduce it to zero (chemical polarisation).

8. The change of temperature in a part of the circuit is determined by the galvanic heating, by the absorption of heat at the places of contact, and by the chemical heat. These changes of temperature lead to the production of fresh differences of potential (thermic polarisation).
R. R.

Application of the Second Proposition of the Theory of Heat to Chemical Phenomena. By A. HORSTMANN (*Ber.*, 14, 1242—1250).—After referring to his own experiments (*Ber.*, 9, 1625), this Journal, 1877 [i], 433), and to those of Isambert (*Compt. rend.*, 92, 919), on the dissociation of a solid into two gaseous products, the author points out that by means of the formula $Q = ATu \frac{dp}{dT}$, the heat

of formation of the dissociated compound may be calculated from the tension of its vapour at the temperature T ; Q = the amount of heat absorbed; p = the vapour-tension; T = the temperature calculated from the absolute zero; A = the mechanical equivalent of heat $\frac{1}{4\frac{1}{2}}$.

If we neglect the volume occupied by the original solid, then u (the increase of volume by the decomposition) = mv , if v = the volume of the molecular weight, m of the gaseous products. For the differential $\frac{dp}{dT}$, we may use the difference of two vapour-tension determinations,

divided by the difference between the temperatures at which they were made, $\frac{p_2 - p_1}{T_2 - T_1}$, the difference of temperature being small. The mean values of p' and p'' , also of T' and T'' can be used for p and T .
W. C. W.

Temperature of Ignition of Gaseous Mixtures. By MAILLARD and LE CHATELIER (*Compt. rend.*, 91, 125—828).—Two methods were adopted for determining the temperature of ignition. (1.) By comparing the volumes of detonating gas and of air, which at the same temperature would fill a porcelain pyrometer. (2.) By placing side by side in a furnace an air pyrometer and a porcelain tube, through which passes the gaseous mixture. The first method is applicable to mixtures which condense after explosion; the latter to those in which there is no change of volume. Mixtures of hydrogen and oxygen, with or without air or carbonic anhydride, inflamed between 552° and 569°. Carbon monoxide and oxygen detonated at about 647·5°. The temperature of ignition did not vary appreciably when the proportions of carbon monoxide and oxygen were varied, or when nitrogen was added to the mixture, but the addition of carbonic anhydride raised it considerably. It was also noticed that carbon monoxide and oxygen would burn gradually, at a temperature considerably lower than that at which it exploded, such combustion often beginning at 477°, and when mixed with carbonic anhydride at 496°.

In like manner, marsh-gas and oxygen will undergo slow combustion, and when raised to a certain temperature will explode, *after the expiration of a variable time*, which is longer as the temperature is lower; it is obvious, therefore, that there cannot be any well-defined temperature of ignition with these gases. A mixture of 0·7 litre of oxygen and 0·3 litre of marsh-gas exploded after a few seconds, at 650°. At 600° no explosion took place, but the mixture underwent slow combustion; when the proportions of the gases were reversed, explosion resulted between 640° and 660°, whilst the addition of 90 per cent. of air raised the required temperature to 730—790°.

Pure marsh-gas when heated alone to 770° is not decomposed, but at 962° it slowly increases in volume by 30 per cent., which then remains stationary. From these experiments it is tolerably certain that the detonating point of marsh-gas is not higher than 790°, and that combustion can take place at much lower temperatures. These results are in opposition to the experiments of Davy, who found that a mixture of marsh-gas and oxygen would not explode by the intervention of an iron rod heated to whiteness; the authors explain the anomaly by showing that the action is slow, and that the gases do not remain long enough in contact with the heated iron to acquire the property of exploding; if, on the contrary, they were steadily heated in an iron crucible, supposing such an operation to be possible, instead of having a white-hot rod plunged into them, they would explode at a red heat, without any trouble.
J. W.

Supposed Heating of Ice. By A. WÜLLNER (*Ann. Chim. Phys.* [2], 13, 105—110).—The author has repeated, by means of a modified

form of apparatus, the experiment described by Carnelley (*Nature*, Feb. 10th, 1881, 341), and finds that *so long as the bulb of the thermometer is completely surrounded by dry ice its temperature does not reach 0°*. If the thermometer rises higher, either the bulb is no longer quite covered with ice, or it is surrounded with water, along with a thicker ice layer. The course of the experiment in other respects was exactly as described by Carnelley. When the bulb becomes partially bare of ice, the thermometer rises even to 50° before the ice becomes detached, and by rapid heating would probably rise considerably higher. The detached ice, when it comes in contact with the hot glass, dances about like Leidenfrost's drops.

In order that fusion may not take place, it is necessary that the ice be not too thick, but how thick was not determined. In one experiment in which the thermometer bulb was surrounded by a coating of ice of 1 to 1.5 cm. thick, and strongly heated with the flame of a Bunsen's burner, the temperature quickly rose to 0°, when fusion commenced, *not, however, on the surface, but in the centre of the ice, and in such a way that the water was forced out through the surface in small drops*, like blisters, and these on removing the lamp instantly froze. On re-heating, the same phenomenon was repeated several times.

In a quantitative experiment, in which 75 grams of ice were kept under low pressure, and exposed to the temperature of steam from boiling water for five hours no fusion occurred, and 42 grams of ice had volatilised into the condenser.

T. C.

Thermochemical Investigations. By C. v. THAN (*Ann. Chim. Phys.* [2], 13, 84—105).—The method previously proposed (*Ber.*, 10, 947) for determining the heat of combustion of gases at constant volume by the use of Bunsen's ice calorimeter, can only be considered as approximate, since several sources of error were overlooked. In the present communication a method is described in which these errors are avoided, and very exact results are obtained in the case of the combustion of hydrogen in oxygen. As a result of the experiments it is found that 1 litre of ($H_2 + O$) gas, measured under normal conditions, when burnt at a constant volume, and completely condensed to water at 0°, evolves a quantity of heat sufficient to melt 2,503,634 grams of ice, with a probable error of + 0.02 per cent.; 1 gram of hydrogen, therefore, when burnt at constant volume, equals 419,273 ice-calories, or 427,789 ice-calories when burnt under constant pressure. This agrees very nearly with the values obtained by Schuller and Wartha (*Ann. Chim. Phys.*, 2, 378, 1877), viz., 418,815, and 427,326 respectively.

Berthelot's statement (*Compt. rend.*, 40, 1241) that the same result is obtained whether the ($H_2 + O$) gas is burnt under constant pressure or at constant volume, is incorrect, the difference in fact amounting to as much as 2 per cent.

T. C.

Study of the Explosive Properties of Mercury Fulminate. By BERTHELOT and VIEILLE (*Ann. Chim. Phys.* [5], 21, 564—574).—The authors' experiments in connection with this subject turn upon the following points:—(1.) The nature of the products of explosion.

(2.) The heat disengaged during explosion. (6.) The density of the fulminate. (4.) The pressure developed during explosion in closed vessels, under varying conditions. The explosion of the fulminate was effected within a steel bomb or eudiometer made for the purpose. The charge, wrapped in tin-foil, was suspended in the centre of the apparatus, and was fired by igniting in contact with it a fine platinum wire by electricity. The eudiometer was first filled with nitrogen at a known temperature and pressure. After the explosion the volume of the gases produced was measured, and an analysis made. In five experiments, the number of c.c. of gas obtained from 1 gram of fulminate varied between 230 and 238 c.c.; the theoretical number being 235.8 c.c. Its analysis gave the following results:—

HCN + CO ₂ .	CO.	N.	H (error).
0.15	65.70	32.28	1.87 = 100.00

From these figures it will be seen that the fulminate decomposes according to a very simple reaction into carbon monoxide, nitrogen, and mercury,



The detonation of the fulminate does not produce, under the above experimental conditions, any substance capable of undergoing sensible dissociation: consequently no gradual combination can subsequently result which might moderate the pressure of the gases or diminish the violence of the initial shock; on the other hand, it is probable that the explosion would be even more sharp and sudden than it actually is, were it not slightly tempered by the condensation of vapour of mercury.

Heat Produced.—By conducting the experiments with the eudiometer immersed in the water of a calorimeter, it was easy to ascertain the amount of heat evolved on explosion. As a mean of five concordant results, 1 gram evolved 403.5 thermal units, a number to which $\frac{1}{50}$ th should be added in order to take into account the small amount of mercury vapour present. This figure calculates for one molecule in grams to +116 units at constant volume, or +114.5 units at constant pressure; a quantity of heat which would be capable of raising all the products, supposing them to be already gaseous, to about 4,200°.

Heat of Formation.—It is easy to deduce from the foregoing the heat of formation of mercury fulminate from its elements, C₂ (diamond) + N₂ + O₂ + Hg (liq.) = C₂N₂HgO₂, absorbs 51.6—114.5 = -62.9 units.

This quantity is negative, as might be expected. The disengagement of heat in the decomposition of the fulminate arises, then, from two causes: (1) the separation of the elements; (2) the simultaneous combustion of the carbon by the oxygen, with production of carbonic oxide. When the fulminate is mixed with chlorate or nitrate of potassium, the carbonic oxide is converted into carbonic anhydride, and the amount of heat disengaged is double that produced by the pure fulminate; the initial shock is, however, so far tempered and moderated by the phenomena of dissociation, due to the carbonic

anhydride, that the mixed fulminate is less violent in its ultimate effects.

The density of mercuric fulminate was found to be 4.42.

Tension Exerted in Closed Vessels.—This was measured by means of the well-known "crusher gauge" devised by Noble, applied in a special apparatus, which is described at length and illustrated by a diagram in the original memoir. The results are compared by introducing into the same receptacle increasing weights of the explosive substance; and the ratio of the weight of the explosive to the internal volume of the vessel is called the "density of the charge."

Density of the charge.	Weight of fulminate.	Pressure in kilos. per sq. cm.
1	2.43 grams.	477
2	4.86 "	1730
3	7.39 "	2697
4	9.72 "	4272

In the last experiment the steel piston was broken into several pieces, and the copper washer was forced out in the form of a thin leaf into the space of $\frac{1}{100}$ mm. existing between the piston and its concentric canal. These phenomena are characteristic of the violence and rapidity of the decomposition by detonation.

But although the local action is more violent with the fulminate than with other explosive materials, it is not right to conclude that the mean pressures developed by the combustion of a charge of given weight are greater also. In fact the contrary is the case. With gun-cotton, Sarrau and Vieille obtained under similar conditions—

Density of the charge.	Pressure in kilos.
1	1085
2	3120
3	5575
4	8745

results which are, moreover, in accordance with the data concerning the quantities of heat and the volumes of the gases produced by the two explosive agents. Similar results obtain when mercuric fulminate is compared with dynamite, the actual pressure developed being only 75 per cent. of that produced by the latter substance or by nitro-glycerol.

The superiority of the effect of the fulminate is mainly due to three causes, viz., the instantaneous character of its decomposition by simple ignition; the almost total absence of dissociation among its gaseous products; and its great density. By reason of these conditions the definite products of the reaction seem to be formed all at once, before the matter has had time to acquire a volume sensibly greater than that which it occupied in its primitive state. If then the fulminate detonates in a receptacle, and in contact with its walls, it develops against the latter at the first moment an instantaneous pressure having no relation to the mean pressure, which is necessarily regulated by the capacity of the recipient. Thus the fulminate, under its absolute density of 4.42, would appear to develop by contact or pressure equal

to 48,000 atmospheres; whilst gun-cotton, compressed to a density of 1.1, would develop only 24,000 atmospheres. Similar experiments and calculations will show that no explosive substance known gives by contact an instantaneous pressure in any way comparable to that produced by the sudden detonation and decomposition of the metallic fulminates.

J. W.

Vapour-densities of Homologous Ethers. By O. SCHUMANN (*Ann. Phys. Chem.* [2], 12, 40—65).—The paper relates to the class of compound ethers formed by the alcohol-radicle salts of organic acids. The apparatus employed was similar to that described by Städel and Hahn (*Annalen*, 195, 218). The numerical results are given in a series of tables, and among the general conclusions drawn from them are the following:—For these ethers an exact accordance with Kopp's law of the boiling point at the pressure of 1 atm. is not found. The tension-curves cannot always be represented by Biot's interpolation formula with three constants. Increase of the molecular weight of the acid with a simultaneous and equal decrease of that of the alcohol acts in the same sense as an increase of the molecular weight of the whole compound; that is, the acid influences the form of the tension-curve more than the alcohol does. The author finds that his results are in complete accordance with a formula given by Winkelmann (*Ann. Phys. Chem.* [2], 9, 208 and 358) for expressing the relations between the temperature and pressure of a saturated vapour.

R. R.

Tension of Aqueous Vapour in Presence of Different Hygroscopic Bodies. By W. MÜLLER-ERZBACH (*Ber.*, 14, 1093—1096).—The relative dehydrating power of two hygroscopic bodies was determined by enclosing the substances for several days in a tube containing air, and then ascertaining which of the two had increased in weight. The following are the results of the experiments:—

Phosphoric anhydride, sulphuric acid, sp. gr. 1.84, and dry potassium hydroxide are equally powerful in attracting water. Sodium hydroxide and calcium chloride attract moisture with almost equal force.

Sodium hydroxide can be completely dehydrated if it is left in a closed vessel containing potassium hydroxide.

W. C. W.

Compressibility of Oxygen; Action of this Gas on Mercury in Eudiometrical Experiments. By E. H. AMAGAT (*Compt. rend.*, 91, 812—814).—Regnault has stated that it is impossible to make an exact experiment respecting the compressibility or dilatation of oxygen, since this gas is absorbed by mercury in appreciable quantity, even during the short time necessary for the experiment. The experience of the author is in direct opposition to this statement; he has distinctly shown that at 14° and at 100° mercury and oxygen, if perfectly pure and dry, can remain in contact for a much longer time than is necessary in any experiment on compressibility, without the slightest action taking place.

Knowing the general accuracy of Regnault's work, the results obtained were surprising to the author himself, but their accuracy was confirmed by a great many concordant experiments which were con-

ducted at varying temperatures below 100°, and between 110 and 420 atmospheres' pressure.

The mean coefficient of dilatation, $\frac{v' - v}{v(t' - t)}$, between 14.7° and 100.2° at varying pressures is as follows:—

	Atm.	Atm.	Atm.	Atm.	Atm.	Atm.
Pressure....	113.4	141.1	181.1	240.9	342.1	418.9
Coefficient..	—	0.00456	0.00469	0.00477	0.00443	0.00407
<i>pv</i> at 100.2°	—	6430	6515	6630	6911	7189
<i>pv</i> at 14.7°..	4638	4626	4648	4711	4993	5336

J. W.

Changes in Volume of some Metals on Fusion. By F. NIES and A. WINKELMANN (*Ann. Chim. Phys.* [2], 13, 43—83).—Of the eight metals (tin, lead, zinc, bismuth, cadmium, antimony, iron, and copper) submitted to investigation, six, viz., tin, zinc, bismuth, antimony, iron, and copper, expand at the moment of solidification, so that the solid is less dense than the liquid metal. No final conclusion could be drawn as regards the two remaining metals, lead and cadmium, although the authors are of opinion that they also expand on solidification.

Quantitative determinations were made in the case of tin, zinc, and bismuth, and it was found that the specific gravity of bismuth is between 1.031 and 1.0497 times as great in the liquid as in the solid state; a sample, whose density was 10.2 in the solid state, assumed a density of 10.77 when melted. For tin and zinc the ratio between the density in the solid and that in the liquid state was also greater than unity, viz., 1.007 and 1.002 respectively.

It is considered probable that experiment will prove that all metals expand on solidification.

T. C.

The Phenomenon commonly called the "Cry of Tin." By J. C. DOUGLAS (*Chem. News*, 43, 203).—If a piece of tin be bent it emits a sound; this, being regarded as a property peculiar to tin, has been termed the cry of tin. The cry of tin is due to crystalline structure; it is not, however, characteristic of tin only, as generally supposed, but may be emitted by zinc and probably by other metals when crystalline in texture. Rolling, in the case of tin and zinc, and probably in other cases, destroys the property with the alteration of texture. If, as supposed, this sound is characteristic of the crystalline structure of metals, it is thought that it may afford a means of great practical use, whereby by the sound a metal emits we may draw conclusions as to its texture, and hence its fitness for certain purposes; or by the sound emitted by a beam when bent we may draw conclusions as to its safety, the microphone or other appliance being called in to aid us where the sounds are exceedingly weak.

D. B.

Determination of Chemical Affinity. By W. OSTWALD. Part IV (*J. pr. Chem.*, 23, 517—536).—The author has fully investigated

nitric, hydrochloric, and sulphuric acids, and calcium and zinc oxalates. The quantity of oxalate which is decomposed increases in a perfectly regular manner with increase of temperature, the curves representing the reactions being nearly straight lines. Only in the case of comparatively concentrated acids was the curvature marked. The influence of dilution is much more complicated than that of temperature, the diluting water forming various hydrates with the acid, and causing decomposition of the oxalates. Curiously the influence of dilution is simplest with sulphuric acid, although formation of acid salts and hydrates might have been anticipated in this case; the action *increases* very regularly as the concentration *diminishes*. In all cases indeed the amount of dissolved oxalate increases with dilution, after a certain point of dilution is reached. Nitric acid dissolves more calcium oxalate as the concentration increases; zinc oxalate, however, in decreasing amounts. At 20° hydrochloric acid dissolves equal proportions of the calcium salts at all dilutions.

The author finds that the law of Guldberg and Waage is not strictly applicable to the calculation of the relative affinity. O. H.

Inorganic Chemistry.

Specific Heat of Chlorine, Bromine, and Iodine Gases. By K. STRECKER (*Ann. Phys. Chem.* [2], **13**, 20—42).—From the experiments detailed in this paper the following conclusions are drawn:—

1. For chlorine, bromine, and iodine, the values of K and γ , and the ratio of the kinetic energy of the progressive motion of the molecules to the total energy are different from those which hold good for other gases whose molecules consist of 2 atoms:—

$$K = \frac{\text{specific heat of the gas at constant pressure}}{\text{specific heat of the gas at constant volume}},$$

referred to water, and γ = the specific heat at constant volume referred to air, the specific heat of air at constant volume being 0.1684.

2. Gaseous chlorine, bromine, and iodine in regard to their thermal behaviour, form a group by themselves among gases whose molecules consist of 2 atoms. In their molecules the atoms seem to have a different reciprocal action from those in the molecules of oxygen, nitrogen, hydrogen, carbonic oxide, nitrogen, and hydrochloric acid.

3. From the behaviour of diatomic gases it is inferred that neither Boltzmann's nor Maxwell's supposition as to the nature of the mobility of atoms in the gaseous molecule has a general validity. T. C.

Solution of Chlorine in Water. By BERTHELOT (*Ann. Chim. Phys.* [5], **22**, 459—464).—The proportion of chlorine dissolved in water varies for the same temperature with the time of contact and

the intensity of light. Thus the author found that a litre of water at 12° dissolves at ordinary pressure 4 grams of chlorine to form a saturated solution; on prolonging the action 6 grams were dissolved. The variations are due to a slow decomposition of water with formation of oxy-acids of chlorine, and this view is further supported by the thermochemical investigations of the author (*Ann. Chim. Phys.* [5], 5, 339).

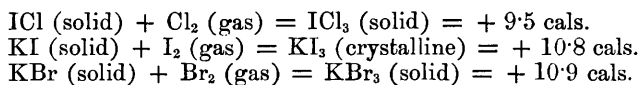
The solubility of chlorine in *concentrated solutions of the metallic chlorides* is less than in water. Thus for 1 litre of the liquid:—

CaCl ₂ 7½H ₂ O saturated with chlorine dissolved	2.45	grams.
MgCl ₂ 7½H ₂ O	2.33	”
MnCl ₂ 5½H ₂ O	2.00	”

but the solubility increases with dilution, when a similar formation of oxy-acids of chlorine can be observed.

But in presence of *concentrated hydrochloric acid* chlorine is far more soluble, and with greater evolution of heat. Thus a solution containing a third of its weight of HCl dissolved 11 grams chlorine, with formation of a pale orange-coloured liquid; whilst the heat evolved in the solution of the gas by a liquid of composition, HCl + 4.5H₂O, was found to be 9.5 cal. (for pure water 3 cal.), a change which corresponds to an equation, HCl (dissolved) + Cl₂ (gas) = HCl₃ (dissolved).

But this heat-evolution is approximately equal to that disengaged in the formation of iodine trichloride from the monochloride, potassium triiodide from potassium iodide, &c. Thus—



Hence it appears that chlorine dissolves in hydrochloric acid, with formation of a hydrogen perchloride of probable formula, HCl₃, analogous to ICl₃, &c. The author also alludes to the great solubility of bromine in hydrobromic acid and of iodine in hydriodic acid.

V. H. V.

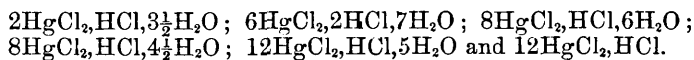
Free Fluorine in Fluorspar. By O. LOEW (*Ber.*, 14, 1144—1146).—The odour of the dark violet variety of fluorspar found at Wölsendorf, the author attributes to free fluorine. In support of this view is cited the formation of fluoride by treatment of the powdered mineral with ammonia. Further its presence may be explained by the fact that the mineral contains cerium fluoride, which on dissociation would yield fluorine and a lower fluoride.

P. P. B.

Action of Hydrochloric Acid on Metallic Chlorides. By A. DITTE (*Ann. Chim. Phys.* [5], 22, 551—566).—The metallic chlorides, as regards the action of hydrochloric acid upon them, are separable into two distinct classes: 1st, those whose solubility increases with increasing quantities of hydrochloric acid present in the solution; 2nd, those whose solubility decreases under the same conditions.

The first class can be divided into two subdivisions: those *soluble*, and those *insoluble* in water.

Soluble Chlorides.—The solubility of these chlorides increases for any given temperature with the concentration of the hydrochloric acid; there are formed at the same time compounds of the salts with hydrochloric acid which are dissociated by water. Thus mercuric chloride forms under various conditions the following compounds—

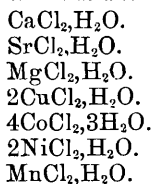


These bodies separate out from the mother-liquors in colourless, transparent crystals, which rapidly become opaque in the air, with loss of water and hydrochloric acid. To the same class belong the chlorides of platinum, gold, bismuth, and antimony, which form the compounds, $\text{PtCl}_4, \text{HCl}$; $\text{AuCl}_3, \text{HCl}$; $\text{BiCl}_3, 8\text{HCl}$; $\text{SbCl}_3, 3\text{HCl}$.

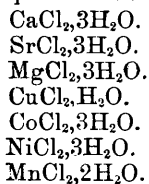
Insoluble Chlorides.—These chlorides, although insoluble in water, are yet dissolved in hydrochloric acid, the solubility increasing with concentration of the acid. To this subdivision belong silver, mercurous and cuprous chlorides.

The second class can equally be divided into two subdivisions:—1st, those which form in concentrated solutions of hydrochloric acid, crystalline hydrates which contain fewer molecules of water than those deposited from an aqueous solution. In the following table are shown the crystalline hydrates so obtained, which are compared with the hydrates deposited from water:—

Hydrochloric acid solution.



Aqueous solution.



2nd subdivision or chlorides, which separate out from hydrochloric acid in the anhydrous state.

To this subdivision belong the chlorides of potassium, sodium, ammonium, barium, and thallium.

V. H. V.

Liquefaction of Ozone in presence of Carbonic Anhydride; its Colour in the Liquid State. By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **91**, 815–817).—When ozonised oxygen, prepared at a very low temperature with special precautions (*Compt. rend.*, **91**, 522), is submitted to a pressure of 200 atmospheres at -23° , in the capillary tube of Cailletet's apparatus, it assumes a blue colour. This colour becomes more intense as the pressure is increased, but the gas shows no signs of liquefaction. If the upper part of the tube is surrounded by liquid nitrous oxide and kept at -88° , the intensity of the coloration augments considerably, and the lower part being maintained at -23° , it is possible to estimate by the eye the difference of

tint, and to see that ozone at -88° is three or four times darker in colour than the same gas at -23° . After a few minutes the temperatures of the two portions of the tube are nearly alike, and the gas is then uniformly coloured deep blue; the ozone is then enclosed in the tube by solid mercury, the meniscus of which remains brilliant, and wholly unattacked by the ozone at this low temperature. Even under these considerations no liquid is formed.

An attempt was made to determine its liquefaction by mixing the ozonised oxygen with a large proportion of carbonic anhydride, and thus to counteract the retarding influence of the uncondensable gas. By steady compression a liquid is obtained, separated from the gas by a meniscus; it is distinctly blue, but its tint does not differ much from that of the supernatant gas. When the pressure is first lessened and then suddenly increased, a column of azure-blue liquid, much more strongly coloured than the gas, collects above the mercury. This is explained by supposing that the mist which is produced on suddenly relieving the pressure is composed mainly of liquid or solid ozone: for this substance is then cooled to a temperature below its critical point,—and that the abundant liquefaction of the carbonic anhydride produced by the subsequent compression collects a portion of this ozone. That this is probably the case is shown by the fact that the coloration of the liquid diminishes, the liquid and the gas acquiring in a few minutes the same shade of colour; the ozone dissolved at first by the carbonic anhydride has then diffused, since the atmosphere of the tube is not saturated with the vapour of ozone.

From the foregoing facts it may be predicted that liquid ozone of a very deep blue colour should be obtained by compressing at a very low temperature the mixture of ozone and oxygen prepared at -88° , since the proportion of ozone in this gas amounts, according to the authors' estimate, to as much as 50 per cent.

The colour of ozone both in the gaseous and liquid condition has enabled its presence to be detected in the products resulting from the decomposition of carbonic anhydride by the inductive discharge. When these gases are compressed in Cailletet's apparatus at -23° , the undecomposed carbonic anhydride liquefies; but instead of being colourless, it is very decidedly blue; this colour is no doubt attributable to the presence of ozone.

J. W.

Sulphuretted Hydrogen Apparatus. By P. HART (*Chem. News*, 43, 191).—The apparatus consists of two test-tubes, the larger of 1 inch internal diameter, the other of such smaller diameter as to slide easily without friction into the larger. This smaller tube is, by means of the blowpipe, perforated at the bottom with a quarter-inch hole, and is also provided with a rubber stopper and a gas-leading tube bent twice at right angles. The larger tube has a piece of rubber tube 2 inches in length, and of rather smaller diameter than itself, pushed over its mouth, 1 inch on the tube and 1 inch projecting. To work the apparatus, fill the larger tube from one-third to one-half full of a mixture of sulphuric acid and water (1 : 3). Drop a lump of iron sulphide into the smaller tube; insert the stopper with the leading pipe firmly into this; and thrust its lower perforated end through the

rubber mouth of the larger tube, pushing it down until it reaches the acid, and allowing sufficient of this to enter the perforation to cover the sulphide of iron. Gas is evolved and can bubble through the solution to be examined. When sufficient has been obtained, raise the upper tube until the lower end is out of the acid. D. B.

Action of Potassium Nitrite on Ammonium Chloride. By D. TOMMASI (*Chem. News*, **43**, 244).—If 10 grams potassium nitrate are melted in a porcelain crucible and then a small quantity of ammonium chloride is added, this salt will begin to rotate with a variable velocity, and then take fire and burn with a violet-purple flame accompanied by a feeble detonation. With ammonium sulphate the phenomenon is more striking, but only very small quantities should be used, or the experiment will become dangerous on account of the projections. The author is examining the nature of the gases evolved, and when the analyses are finished he will endeavour to explain these reactions. D. B.

Action of Chlorine and Hydrochloric Acid on Lead Chloride. By A. DITTE (*Ann. Chim. Phys.* [5], **22**, 566–573).—If hydrochloric acid is added to an aqueous solution of lead chloride, and a current of chlorine passed in while the temperature is kept constant, the lead chloride slowly dissolves, the liquid acquires a yellowish-red colour, and the quantity of hydrochloric acid present is increased. On addition of three or four times its volume of water to the liquid so obtained, a copious precipitate of lead peroxide is thrown down. The author adduces some experiments to establish the increase of hydrochloric acid formed and of lead chloride dissolved. These changes are more marked if silver nitrate is added to the original liquid. It is most probable that the phenomena are exactly analogous to those examined by Berthelot in his study of the action of chlorine on manganese chloride (*Compt. rend.*, **91**, 251), and in both cases there is formed a hydrochloride of the metallic perchloride, which is dissociated by water into free chlorine and hydrochloric acid. This dissociation increases rapidly with rise of temperature; but on the other hand if the original liquid be further charged with hydrochloric acid, it will be found that, although the quantity of hydrochloric acid is increased by the passage of the chlorine, yet the quantity of lead chloride dissolved decreases. This result is explained by supposing that the hydrochloride of the perchloride reaches its maximum of formation, and then diminishes gradually; and in fact it is proved by experiment that a saturated solution of lead chloride in hydrochloric acid is unaltered by the passage of the chlorine.

Again, by the action of hydrochloric on lead peroxide, similar yellow-coloured liquids are obtained, which, on warming, are immediately decomposed into chlorine and lead chloride, and from which lead peroxide may be precipitated by water. V. H. V.

Note.—The author seems to be quite unaware that most of the phenomena here detailed have already been described and explained by practically the same hypothesis. (Fisher, this Journal, Trans., 1879, 282–285).—V. H. V.

Lead Chlorobromide. By M. W. ILES (*Chem. News*, **43**, 216) — In the treatment of the Leadville carbonate ores by the blast furnace, the author has noticed a number of very curious and interesting compounds. Recently a compound having the formula $\text{Pb}(\text{BrCl})$ has been discovered occurring as a furnace product in small circular openings in the cast-iron supporting plate, $11\frac{1}{2}$ inches above the water-jacket. The furnace crystals occur in several forms, as, for example, in pure white, delicate, dendritic plates, not unlike crystals of lead chloride; in long acicular needles; in semi-fused distorted needles having a slightly yellowish tint; and in entirely warty masses. They dissolve in warm water, the aqueous solution depositing plate-like crystals. A white coating is obtained when the crystals are sublimed on charcoal. On heating in a closed tube, they melt readily to a bright red mass; which lightens up on cooling, changing from a yellow to a pure white. When the heat is increased the compound sublimes in heavy oily drops. Sp. gr. 5.741. The compound is decomposed by boiling concentrated sulphuric acid only on repeated application, and the complete transformation into a sulphate is difficult. Analysis gave:—

	Found.	Calculated.
Pb	63.729	64.186
Br	25.321	35.814
Cl	10.345	

corresponding with the formula $\text{Pb}(\text{BrCl})$.

D. B.

Crystalline Form of Iron-manganese (Spiegeleisen). By E. MALLARD (*Jahrb. f. Min.*, 1879, 617).—The author examined numerous products containing from 11—55 per cent. manganese. Between 11 and 52 per cent. the form remains the same, viz., rhombic, $\infty\text{P}\infty$ and ∞P ($= 112^\circ 33'$); $\infty\text{P}\infty$ generally predominates, and the faces striated by its oscillatory combination with ∞P end in undefined pyramidal-like points. Between 52 and 55 per cent. manganese, the form suddenly changes to apparently hexagonal prisms, but really a rhombic prism of nearly 120° with $\infty\text{P}\infty$. The crystals have invariably the same composition as the whole mass from which they separated: thus, no separation of an iron manganese having a definite formula has taken place, and it is difficult to account for this sudden change of crystalline form, accompanied by only a gradual change in composition.

H. B.

Oxides of Manganese. By S. U. PICKERING (*Chem. News*, **43**, 189, 201, 213, and 225).—The following is a summary of the more important facts indicated by the author's experiments:—

1. A perfectly pure hydrated oxide of manganese may be obtained by the decomposition of manganese sesquichloride with excess of water; this oxide, however, does not contain the amount of oxygen theoretically contained in the dioxide.

2. In the oxides investigated, both pure and impure, the manganese present as dioxide bore to that present as monoxide ratios varying between 0.494 and 7.423, and they all (eight in number), with one exception, experienced an alteration in composition when heated to

100° or 200° C. In six out of the seven cases this alteration was due to an evolution of oxygen, in the seventh case to an absorption of that gas. In all the cases investigated, where any change took place at 100°, this change was increased at 200°, but beyond this the extent of the loss at 100° does not afford any criterion as to what the loss at higher temperatures will be.

3. The results obtained with oxide No. 1 (pure manganese dioxide), where experiments were made at six different temperatures, when represented diagrammatically, form a curve of considerable regularity.

4. The composition of the oxide taken is by no means the main factor in determining its behaviour on heating; the poorest oxide was not the one which experienced the greatest gain. The amount of the alteration is greatly dependent on the amount of water present in the sample. The oxides in which by far the greatest loss of oxygen took place were those examined at once after their preparation, and while still in an undried condition.

5. In the one case, however, where the same oxide was examined both before and after being dried, the loss experienced at 100° was practically identical.

6. Whatever alteration took place was found to be practically complete in between half an hour and an hour and a half after the oxide had become mechanically dried. Oxide No. 1 experienced no alteration on being kept in boiling water for some hours. On repeatedly moistening and heating it, the gain of oxygen at 100° was greatly increased. When heated in dry air at 100° it absorbs five times as much oxygen as when heated at the same temperature in air of $\frac{1}{60}$ hygrometric state.

7. In the case of oxide No. 5 (this was pure dioxide of manganese, which, being washed, was dried in an air-bath at 29—40° C., subsequently ground in a mortar and shaken through fine cambric in order to reduce it to as fine a powder as possible) a considerable loss of oxygen was observed when it was heated in boiling water, this loss being complete in two and a half hours. When heated at 100° in dry air instead of in partially moist air, the loss of oxygen was nearly doubled.

8. The oxides of manganese appear to undergo a molecular change on being kept in air for some length of time, whereby their behaviour on being heated is entirely reversed, a gain of oxygen instead of a loss taking place. This molecular alteration is unaccompanied by any change in composition.

9. On heating small quantities of manganese oxides in a platinum dish over a Bunsen burner, the oxides obtained were found to be remarkably constant in composition, always containing rather more manganese than the sesquioxide does when the gas was at the day pressure. With a larger supply of gas less constant results were obtained, and some of these showed that a reduction considerably beyond Mn_2O_3 could in this way be obtained.

10. Wright and Menke and Veley confirm the present results in showing that a loss or gain of oxygen takes place at about 200°, but they fail to show any alteration of temperature as low as 100° (the heating being performed in air). They show that the oxygen value is

not in the main dependent on the richness of the sample taken, for the richest specimen suffered no loss at all at 210° , whilst poorer ones lost nearly 3 per cent. of their total available oxygen. The fact that the richest specimen lost no oxygen is probably due to its being nearly anhydrous.

11. The amount of water retained by the oxides at 100° and 200° is very variable; that retained in drying them in partially moist air at 200° is, according to the present experiments, 3 to 6 per cent.; according to other authorities, the use of a current of perfectly dry air reduced it to 0.7 to 1.7 per cent.

D. B.

Spontaneous Oxidation of Mercury and other Metals. By BERTHELOT (*Bull. Soc. Chim.* [2], **35**, 487—491).—It is generally supposed that mercury dissolves the oxygen of the air, and is slowly oxidised at ordinary temperatures, although the evidence on this point is far from conclusive. The author has made a series of experiments to determine the conditions of the oxidation of mercury in the pure state, and in the presence of acids and of alkaline metals. It was found that, when mercury was exposed to laboratory air, a thin pellicle was formed on the surface after about two days, and was continually renewed after removal. The presence of mercurous oxide in the pellicle was ascertained by solution in hydrochloric acid and the blackening of the resulting mercurous chloride by ammonia. This slow oxidation takes place even in presence of a limited volume of air. In exactly the same way the surfaces of lead, iron, copper, tin, &c., are superficially oxidised, the oxidation being limited by the difficulty of renewing the surface, and the preservation of the metal by the film of oxide formed. These results are completely in accordance with thermochemical data, as an immediate consequence of which it follows that the reaction will take place more easily and more completely in presence of some reagent which is capable of combining with the metallic oxide, with evolution of heat. Thus, when mercury is placed in contact with hydrochloric acid in presence of air, it is immediately covered with a white coating of the protochloride. The probable explanation of the reaction is that the mercury is at first oxidised, and then converted into chloride, and the perpetual recurrence of these two changes assists the chlorination of the mercury. In exactly the same manner silver or copper is converted into the chloride when exposed to hydrochloric acid or sodium chloride. The formation of the hydrocarbonate of lead and of verdigris is probably due to analogous changes.

V. H. V.

Isodimorphism of Arsenious and Antimonious Oxides. By GUENGE (*Jahrb. f. Min.*, 1879, 621—622).—The author has attempted to prepare the rhombic modification of arsenious acid by Debray's method, viz., sublimation at a high temperature; but the long pointed crystals, formed on long-continued heating only, consisted of a series of octohedrons, united together along one of their axes. The effect of an increased pressure of air in the experimental tube favours the growth of large single octohedrons.

H. B.

Preparation of Platinum. (*Dingl. polyt. J.*, **240**, 213—217.)—Matthey (*Iron*, 1879, **13**, 654 and 678) describes the preparation of pure platinum and the production of platinum-iridium. The commercial alloy is fused with six parts by weight of pure lead, then gradually dissolved in dilute nitric acid (1 : 8). Thus the greater part of the lead is brought into solution, besides copper, iron, palladium, and rhodium; these are separated from the solution in the usual manner. The residue containing platinum, lead, and iridium, is treated with dilute *aqua regia*, the platinum and lead being dissolved, leaving impure iridium in the residue. The lead is converted into sulphate by treatment with sulphuric acid and evaporating, and the platinum chloride extracted from the residue with distilled water. The solution is then treated with an excess of chloride of ammonium and sodium, heated to 80°, and allowed to settle for a few days. The precipitate is then washed intermittently with a saturated solution of ammonium chloride and with water acidulated with hydrochloric acid, in order to separate rhodium, and is finally dried and ignited to dull redness with potassium pyrosulphate and ammonium sulphide.

The platinum is reduced and remains in the melt in a perfectly pure state. It is free from all traces of rhodium and other metals, and has the highest sp. gr. obtainable, viz., 21.46. The iridium residue containing traces of platinum, rhodium, ruthenium, and iron, is dried and fused with ten times its weight of lead. The latter is then dissolved in nitric acid, and the residue treated for some time with *aqua regia*. A crystalline mass is obtained, consisting of the corresponding compounds of iridium, rhodium, ruthenium, and iron. The rhodium is separated as rhodium potassium sulphate by strong ignition with potassium pyrosulphate. The residue is fused with ten times the weight of potassium hydroxide and three times the weight of nitrate, which converts the iridium and ruthenium into the corresponding potassium salts, and oxidises the iron. The cold melt is treated with cold water, the residue consisting of potassium iridiate. The latter is washed with water, containing potassium hydroxide and sodium hypochlorite until the filtrate is colourless, then with distilled water. The residual blue powder is then treated with an aqueous solution of sodium hypochlorite, and distilled until the distillate is no longer coloured red when treated with alcohol and hydrochloric acid. The residue is further treated with water containing alkaline sodium hypochlorite in order to remove the last traces of ruthenium. The blue powder (iridium oxide) is dissolved in *aqua regia*, evaporated to dryness, taken up with water, and filtered. The dark-coloured solution is poured into a concentrated solution of sodium hydroxide mixed with sodium hypochlorite and distilled in a current of chlorine. The distillate should not show any ruthenium reaction when treated with alcohol and hydrochloric acid. The residue is then reduced to oxide of iridium by a mixture of carbonic oxide and anhydride evolved from oxalic and sulphuric acids (not oxide of iron) and heated to redness with potassium pyrosulphate, which removes the last traces of iron and rhodium. It is washed with distilled water, then with chlorine water (to remove gold), and finally with hydrofluoric acid to remove silicic acid. The iridium is said to have a sp. gr. of 22.39 after fusion;

but even when prepared with all possible care, it always contains minute traces of oxygen, ruthenium, rhodium, and iron, and has a maximum sp. gr. of 22·38.

To prepare the platinum-iridium alloy Matthey fuses 450 ounces of platinum, together with 55 ounces of iridium, and pours the mixture into a suitable mould. The resulting casting is broken up, fused with a strong blast of oxygen and coal-gas, and hammered out at a white heat under the steam hammer; it is then rolled, broken up into small bars, again fused, and finally left to cool. The mass obtained is perfectly homogeneous, free from cracks and air bubbles, has a sp. gr. of 21·516, and gives on analysis—

	Pt.	Ir.	Rh.	Ru.	Fe.	
I	89·40	10·16	0·18	0·10	0·06	= 99·90
II	89·42	10·22	0·16	0·10	0·06	= 99·96

Busch prepares an alloy which approaches gold in colour, and is very elastic, from 9 parts fine gold and 1 part platinum. A mixture of 4 parts platinum, 3 parts silver, and 1 part copper, forms an alloy used for metallic pens.

Daubrée attributes the magnetic properties of refined platinum to the presence of traces of iron. According to Reichardt, silicon is said to injure platinum, 0·001 silicon rendering it brittle. D. B.

Organic Chemistry.

Action of Ammonia on Isobutyridene Chloride. By S. ECONOMIDES (*Compt. rend.*, **92**, 1235—1238).—Isobutyridene chloride was heated with four and a half times its volume of alcoholic ammonia saturated at 12° for five days at 200—220°, and for some time at 240°. After separation of ammonium salts the liquid was distilled, when ammonia was given off and chlorisobutyridene was obtained in considerable quantity. Hydrochlorides of various bases were also formed. In many cases alcoholic ammonia might probably be substituted with advantage for alcoholic potash. For example, 40 grams dichloropropane (methyl-chloracetol) heated at 200° with alcoholic ammonia gave about 20 grams of chlorpropylene.

When chlorisobutyridene is mixed with hypochlorous acid, the compound $C_4H_7Cl(OH)Cl$ is obtained as a colourless, limpid liquid with an ethereal odour; sp. gr. at 0 = 1.0335; b. p. 143.5° under a pressure of 764 mm.

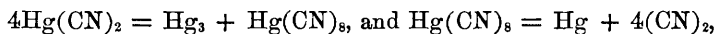
C. H. B.

Action of Sodium and Carbonic Anhydride on Allylene Chloride. By A. PINNER and W. SCHAUMANN (*Ber.*, **14**, 1081—1082).—When carbonic anhydride is passed through a mixture of equal parts of benzene and allylene chloride containing thin slices of metallic sodium, the sodium salt of tetrolic acid, $C_4H_4O_2$, is produced. This acid combines directly with 4 atoms of chlorine or 2 atoms of

bromine. The bromine cannot be eliminated from the dibromocrotonic acid without liberating carbonic anhydride. W. C. W.

Decomposition of Mercury and Silver Cyanides. By E. J. MAUMENÉ (*Bull. Soc. Chim.* [2], **35**, 597—598).—It is well known that mercury cyanide is not simply decomposed into cyanogen and mercury, but that there is always left behind a brown bye-product, considered to be paracyanogen.

The author considers that the change may be represented by the equations—



and that the molecule of paracyanogen is C_4N_4 . It was found experimentally that at 320—400 mercury is disengaged without the slightest trace of cyanogen, but at a slightly higher temperature cyanogen is given off in abundance. The decomposition of silver cyanide may probably be expressed by similar equations. On triturating with mercury the residue left after the evolution of the first few bubbles of cyanogen to remove the silver, and on subsequent treatment with 1.4 nitric acid, a compound of silver with paracyanogen, $\text{Ag}(\text{CN})_4$, may be extracted containing 50 per cent. of the metal. V. H. V.

Oil of Wine. By E. C. HARTING (*J. pr. Chem.* [2], **23**, 449—480).—After noting the results obtained by previous investigators with the oily liquid obtained from small preparations of ether or ethylene, the author gives an account of his examination of the products from the manufacture of ether on a large scale. In the technical conversion of alcohol into ether by sulphuric acid, the vessels are kept in uninterrupted use for four weeks, during which time about 800 kilos. of alcohol are used. After the ether is distilled off, the residue consists of a tarry substance, which is a high condensation-product examined by Marchand (*Berz. Jahresber.*, **19**, 504), and a liquid.

The liquid, freed from sulphuric acid, ether, alcohol and water, has a neutral reaction. Sp. gr. 0.903 at 17.5°. It is clear, yellowish, of a sweet taste, and is not decomposed even on boiling with water or alkalis; it does not contain sulphur, nor does it deposit crystals on cooling to 0°. The liquid was submitted to systematic fractioning, by Linnemann's method, and each fraction examined separately.

Fraction boiling at 112—113°, gave numbers agreeing with the formula $\text{C}_7\text{H}_{10}\text{O}$, and from its behaviour with hydriodic acid and the analysis of the iodides, was found to be ethylamyl oxide.

Fraction 150—160. After shaking up with hydrogen sodium sulphite, removing the sodium compound and distilling, a colourless mobile liquid, with camphor-like odour, was obtained (b. p. 153—155°), insoluble in water, soluble in alcohol; sp. gr. 0.8405; it yielded on reduction a secondary alcohol (b. p. 163—165°), $\text{C}_8\text{H}_{18}\text{O}$, with a musty odour, and forming a crystalline compound with calcium chloride; and on oxidation valeric and propionic acids were formed; it was therefore "ethylamylketone."

The sodium sulphite compound gave "methylhexylketone" (b. p.

163—165°), recognised by its breaking up into caproic and acetic acids on oxidation.

In another instance, besides the two ketones, a hydrocarbon was obtained (b. p. 156·5—158°), which on examination of the bromine-compounds obtained from it, proved to be "rutylene."

The other fractions contain mixtures of these bodies, as well as another hydrocarbon, ether, and ketone.

This product from the preparation of ether on a large scale is quite different from those examined by previous workers. D. A. L.

T. Thomsen's Law of Multiple Rotations. By H. LANDOLT (*Ber.*, **14**, 1048—1053).—A further criticism of T. Thomsen's experiments on specific rotation and the results deduced from them.

W. C. W.

Reduction of Cupric Hydrate Oxide in Neutral and Acid Mixtures by Grape-sugar. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv*, **22**, 346—353).—Hydrated cupric oxide is not reduced by digestion with sugar solution at 20—50°, but is reduced by continued boiling. The filtrate still contains copper, generally in combination with some oxidation product of the sugar. The sugar does not act on these compounds of cupric oxide in the absence of alkali. If the hydrated oxide is precipitated by alkali in a mixture of cupric sulphate and sugar, the grape-sugar exhibits a reducing action even in the cold. Cupric acetate is also reduced in the cold, but the action is not complete.

W. N.

Reduction of Cupric Hydrate in Alkaline Liquids. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv*, **22**, 354—373).—The authors find that for the reduction of 5 mols. of cupric oxide by 1 mol. of sugar, only 1 mol. of alkali (soda) in excess is necessary, provided the mixture is boiled for an hour. The reduction goes on faster in the presence of 2 mols. in excess of alkali. Under these circumstances 1 mol. of sugar is capable of reducing 5·5 mols. cupric oxide. The lower the temperature the more alkali is necessary, and, as a rule, reduction is not complete at temperatures below 90°. The authors also find that the sugar is decomposed by the alkali not only at the boiling point, but also in the cold, and the more so the stronger the alkali; hence they recommend, in applying Trommer's test, the use of weak solutions of alkali.

W. N.

Decompositions which occur in the Use of Trommer's Test. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv*, **22**, 391).—The authors are of opinion that the reduction of the copper solution is brought about by the sugar directly, and not indirectly by a product of the action of the alkali on the sugar.

W. N.

Arabinose. By P. CLÄESSON (*Ber.*, **14**, 1270—1272).—The author denies Kiliani's statement (*Ber.*, **13**, 2404; this volume, 243) that arabinose is identical with lactose, and he confirms the accuracy of Scheibler's description (*Ber.*, **1**, 58 and 108; **6**, 612; this Journal, 1873, 1124) of the properties of arabinose. Only those specimens of

gum arabic which yield either very little or no mucic acid on oxidation with nitric acid contain arabinose.

Lactose is not readily attacked by chlorosulphonic acid; arabinose is rapidly decomposed by this reagent. On oxidising arabinose with nitric acid, mucic acid is not formed. W. C. W.

Ketines. By V. MEYER and F. P. TREADWELL (*Ber.*, **14**, 1150).—The authors have obtained a series of volatile bases formed by reducing nitroso-ketones with sodium-amalgam, or with tin and hydrochloric acid. For these bases the name *ketine* is proposed; they all, like chloral, combine with water to form crystalline hydrates. Their general formula for these compounds is $C_nH_{2n-4}N_2$; the platinochloride of *dimethylketine* has already been described by Gutknecht (*Ber.*, **12**, 2292). P. P. B.

Action of Ammonium Cyanate on Aldehydes. By N. LUBAVIN (*Bull. Soc. Chim.* [2], **35**, 557).—The author starts from the hypothesis that in Strecker's synthesis of alanine, the formation of the nitrite of an amidated acid is preceded by that of ammonium cyanate, at the cost of aldehyde-ammonia and the hydrocyanic acid. He has accordingly studied the action of ammonium cyanate on several aldehydes, and has obtained alanine from aldehyde, and leucine from valeraldehyde. V. H. V.

Condensation of Acetone. By A. PINNER (*Ber.*, **14**, 1070—1080).—The acid $C_8H_{13}NO_3$, and the cyanide $C_{11}H_{18}N_2O_2$, which Simpson (*Annalen*, **148**, 351) obtained by the action of potassium cyanide on acetone saturated with hydrochloric acid gas, are best prepared by the following modification of his original process. The impure oil formed by passing hydrochloric acid gas through acetone, is first washed with sodium hydroxide, and then boiled for ten hours in a flask connected with an upright condenser, with 7 parts of alcohol (80 per cent.), and half a part of potassium cyanide. The liquid on cooling deposits the cyanide $C_{11}H_{18}N_2O_2$. The residue which remains when the alcoholic mother-liquor is evaporated to dryness is dissolved in water and filtered. The addition of hydrochloric acid to the aqueous solution slowly precipitates the acid $C_8H_{13}NO_3$, and from the filtrate ether extracts a second acid, $C_7H_{12}O_3$, to which the name *mesitonic* acid is given. The crude mesitonic acid is dissolved in water, the impurities removed by filtration, and the acid again extracted with ether. It crystallises from water in small prisms, and from ether in large transparent plates (m. p. 96°), soluble in alcohol and in benzene. The acid distils between 230° and 240° , without decomposition. Its salts are very soluble in water.

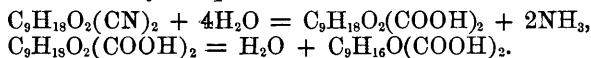
The acid $C_8H_{13}NO_3$ is deposited from an aqueous solution in flat prisms containing 1 mol. H_2O . The anhydrous acid melts at 174° , and at a higher temperature distils without decomposition. Its metallic salts are freely soluble. The ethyl salt crystallises in colourless prisms (m. p. 90°), soluble in alcohol and in dilute acids.

On oxidation with potassium permanganate in an acid solution,

$C_6H_{13}NO_3$ splits up into an indifferent compound, $C_6H_9NO_2$, and an unstable acid, $C_7H_9NO_4$.

The former compound is deposited from an ethereal solution in highly refractive plates, which melt at 106° , but begin to sublime at 60° . The acid melts at $84-87^\circ$, and decomposes at 135° with evolution of carbonic anhydride.

The cyanide $C_{11}H_{18}N_2O_2$, formed according to the equation $3C_3H_6O + 2HCN = C_{11}H_{18}N_2O_2 + H_2O$, crystallises in glistening plates, which melt above 320° . It is not attacked by sodium or potassium hydroxides, but dissolves in hot strong hydrochloric acid, forming an unstable addition product, which is deposited on cooling. If the cyanide is heated for 24–36 hours, with 40 parts of fuming hydrochloric acid, it yields *phoronic acid*, $C_{11}H_{18}O_5$.



Phoronic acid is sparingly soluble in hot water, and freely soluble in alcohol. It is a powerful dibasic acid, forming the following crystalline salts:— $C_{11}H_{17}KO_5 + 1\frac{1}{2}H_2O$ (needles); $C_{11}H_{16}O_5Ca + 3H_2O$ (prisms) and $C_{11}H_{16}O_5Ag_2 + H_2O$.

Ethyl phoronate crystallises in prisms (m. p. 125°), soluble in alcohol. The amide crystallises in colourless prisms, sparingly soluble in alcohol. It melts above 300° .

Phoronic acid melts at 184° , and is at the same time converted into the anhydride, $C_{11}H_{16}O_4$. This body melts at 138° , and distils without decomposition.

The imide $C_{11}H_{16}O_3.NH_3$ forms long needles (m. p. 205°), sparingly soluble in alcohol.

The author believes that phoronic acid, $C_{11}H_{18}O_5$, has the following constitution:— $CMe_2(COOH)CH_2.CMe < \overset{O}{\underset{CH_2}{\text{C}}} > CMe.COOH$.

W. C. W.

Double Salts of the Lower Members of the Acetic Acid Series. Part II. By A. FITZ (*Ber.*, **14**, 1084–1088).—The double propionates of calcium and barium, $2(C_3H_5O_2)_2Ca, (C_3H_5O_2)_2Ba$, calcium and strontium, $2(C_3H_5O_2)_2Ca, (C_3H_5O_2)_2Sr$, and calcium and lead, $2(C_3H_5O_2)_2Ca, (C_3H_5O_2)_2Pb$ (*Ber.*, **13**, 1312; this Journal, 1880, Abstr., 779) are dimorphous. The first of these double salts crystallises in regular octohedrons, and the other two salts in a combination of the quadratic secondary prism and pyramid; but if a solution containing 1 part of the calcium barium double salt and 3 parts of the calcium lead salt is allowed to evaporate, quadratic crystals containing barium are obtained. By reversing the proportions in which the salts are mixed, regular crystals containing lead are deposited.

Calcium and lead propionates also form a second double salt, $4(C_3H_5O_2)_2Ca, 5(C_3H_5O_2)_2Pb + 12H_2O$, which crystallises in a combination of the cube, dodecahedron, and tetrahedron. Calcium butyrate combines with lead propionate to form the compound $4(C_4H_7O_2)_2Ca, 5(C_3H_5O_2)_2Pb + 12H_2O$, which crystallises in a combination of the pyramidal tetrahedron and the dodecahedron. The

magnesium lead propionate and *magnesium barium propionate* have a more complicated composition than that previously assigned to them (*loc. cit.*), and are analogous to the calcium lead propionate, *e.g.*, $4(\text{C}_3\text{H}_5\text{O}_2)_2\text{Mg}, 5(\text{C}_3\text{H}_5\text{O}_2)_2\text{Ba} + 12\text{H}_2\text{O}$, and $4(\text{C}_3\text{H}_5\text{O}_2)_2\text{Mg}, 5(\text{C}_3\text{H}_5\text{O}_2)_2\text{Pb} + 12\text{H}_2\text{O}$.
W. C. W.

Electrolysis of Formic and Mellic Acid. By M. BOUNGUÉ (*Bull. Soc. Chim.* [2], **35**, 561).—The gaseous products formed by the electrolysis of mellic acid consist principally of hydrogen, oxygen, and carbonic anhydride, with hardly any traces of carbonic oxide. In the electrolysis of formic acid, the proportion of carbonic anhydride increases under those conditions which are likely to favour oxidation, *viz.*, the concentration and temperature of the electrolyte, the surface of the electrodes, and the diminution of the intensity of the current. These experiments confirm the view put forward by the author, that in the electrolysis of organic acid there is formed at the positive pole a complex group, which, in the presence of water, generates the original acid with liberation of oxygen; and this in its turn oxidises the reproduced acid.
V. H. V.

Potassium Cyanide and Ethyl Dichloracetate. By A. CLAUS (*Ber.*, **14**, 1066—1070).—A reply to Böttinger's remarks (*Ber.*, **14**, 730).
W. C. W.

Fermentation Normal Valeric Acid. By A. FITZ (*Ber.*, **14**, 1084).—As a further proof of the identity of the acid obtained by the fermentation of calcium lactate and normal valeric acid, the solubility of the calcium salt and the boiling point of the ethyl salt of these acids have been determined.
W. C. W.

Monobromocrotonic Acids (α - and β). By A. MICHAEL and L. M. NORTON (*Amer. Chem. J.*, 1880, **2**, 11—19).*—When bromine (1 mol.) dissolved in carbon disulphide is added to a solution of solid crotonic acid in a large quantity of the same liquid, $\alpha\beta$ -dibromobutyric acid, $\text{CH}_3\text{CHBrCHBrCOOH}$, is formed, which is easily soluble in alcohol, ether, and benzene; sparingly soluble in cold, more freely in hot water; and crystallises from ether in long white needles; and on treating an alcoholic solution of this acid with an alcoholic solution of potassium hydroxide (2 mols.), heating the liquid for a few minutes on the water-bath to complete the reaction, filtering off the potassium bromide which separates, diluting the alcoholic filtrate with 8 or 10 mols. water acidulated with sulphuric acid, exhausting with ether, and removing the ether by evaporation, a *monobromocrotonic acid*, $\text{C}_3\text{H}_5\text{BrO}_2$, remains, which, when purified by repeated crystallisation from water, conversion into barium salt, and separation therefrom by hydrochloric acid, melts constantly at 92° . It is easily soluble in ether, alcohol, and carbon bisulphide, moderately soluble in water, from which it crystallises in long white needles. Its silver salt,

* *The American Chemical Journal*, edited by Ira Remsen. Baltimore, 1879, *et seq.*

obtained by precipitation from the aqueous ammonium salt, crystallises in white needles, not altered by light; the barium and calcium salts are easily soluble, and crystallise in plates, the former with $3\frac{1}{2}$ mols., the latter with 3 mols. H_2O .

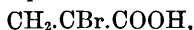
This bromocrotonic acid (distinguished as β) is easily converted by reduction with sodium-amalgam into normal butyric acid, and readily takes up 1 mol. bromine, forming a *tribromobutyric acid*, very soluble in alcohol and benzene, and crystallising from the latter in large, colourless, rhombic plates, melting at 114° . It is not identical with the monobromocrotonic acid which Kekulé obtained (*Annalen*, Suppl. 2, 85) by the action of alkalis on citradibromopyrotartaric acid, inasmuch as Kekulé's acid melted at 65° , was converted by bromine into a tribromobutyric acid crystallising in hard prisms, and by nascent hydrogen, according to Geromont (*Ber.*, 1872, 92) and Swarts *Bull. Belg.* [2], 33, 1), into isobutyric acid.

α -Monobromocrotonic acid is prepared from liquid or α -dibromobutyric acid in the manner above described for the β -acid, excepting that the action is slower, and requires several hours' heating on the water-bath with reversed condenser to complete it. The same acid is formed by treating α -dibromobutyric acid with alcoholic ammonia; also, with evolution of hydrogen bromide, when the α -dibromobutyric acid is heated nearly to its boiling point.

α -Bromocrotonic acid is somewhat soluble in cold water, and much more soluble in hot water, from which it crystallises in long, colourless needles, easily soluble in alcohol, ether, and benzene, less soluble in carbon sulphide. It melts at 106.5° , and decomposes partially on boiling. Its *silver salt*, obtained by precipitation, forms white needles, very sensitive to light, and decomposes in aqueous solution, slowly in the cold, very quickly on boiling, with separation of silver bromide. The *barium salt*, $C_4H_4BrO_2Ba + 2H_2O$, dissolves easily in water, and crystallises in plates. The *tribromobutyric acid* obtained by the action of bromine on α -bromocrotonic acid, dissolves readily in water, and crystallises therefrom in bunches of white needles, melting at 111° ; it dissolves very easily also in alcohol, ether, and carbon sulphide. It appears to be different from the tribromobutyric acid obtained from β -bromocrotonic acid, but the quantity of it obtained was not sufficient for satisfactory investigation.

The constitutional formula of α -bromocrotonic acid depends on that of α -dibromobutyric acid, in which the position of the second bromine-atom has not yet been established, although, judging from the action of bromine on other organic acids, the α -position would seem very probable, that is to say, the formula of this dibrominated acid should be $CH_3.CH_2.CBr_2.COOH$. In this case the α -bromocrotonic acid obtained from it should have the formula $CH_3.CH=CBr.COOH$. If this be the case, there remains for the acid obtained from $\alpha\beta$ -dibromobutyric acid only two formulæ, viz., $CH_3.CBr=CH.COOH$, and $CH_2=CH.CBr.COOH$, the former of which is the more probable of the two. The formation of different bromocrotonic acids from α - and $\alpha\beta$ -dibromobutyric acids, is of considerable interest, inasmuch as Tollens has shown that the α -acid and $\alpha\beta$ -dibromopropionic acids yield one and the same bromacrylic acid.

Tribromopropionic acid, $\text{CH}_2\text{Br}.\text{CBr}_2.\text{COOH}$, is obtained by addition of bromine in molecular proportion to α -bromacrylic acid,



both dissolved in carbon sulphide. It is slightly soluble in cold, more soluble in hot water, and separates therefrom as an oil, which remains liquid as long as it contains a trace of water. A drop of water placed upon the pure acid instantly converts it into an oil. The pure acid is not hygroscopic. It dissolves very easily in alcohol and ether, less easily in benzene, from which it crystallises in needles. It melts at 92° , but a small quantity of impurities lowers the melting point very considerably. Its silver salt is very unstable; the barium and calcium salts are more permanent, and very soluble in water. This tribromopropionic acid is decomposed by alcoholic potash, with formation of an acid, which appears to be a dibromacrylic acid. It does not appear to be identical with the tribrominated acid (m. p. 53°), which Fittig u. Petri obtained (*Annalen*, **195**, 73) by the action of hydrobromic acid upon dibromacrylic acid. H. W.

Action of Potassium Cyanide on Ethyl Chlorisocrotonate.

By A. CLAUS and G. LISCHKE (*Ber.*, **14**, 1089--1093).—Potassium cyanide acts slowly on an alcoholic solution of ethyl chlorisocrotonate at the ordinary temperature. If the mixture is warmed the action goes on more rapidly, and on saponifying the product with potassium hydroxide, potassium tricarballoylate is obtained; but if the reaction takes place at the ordinary temperature, treatment with potassium hydroxide will yield a mixture of tricarballoylic and itaconic acids.

W. C. W.

Lead Plumbothioglycollate. By C. LIEBERMANN and A. LANGE (*Ber.*, **14**, 1265—1266).—The authors confirm the accuracy of Claesson's statement (*Annalen*, **187**, 123) that the lead salt, precipitated on adding lead acetate to an alkaline thioglycollate, has the composition $\text{C}_2\text{H}_2\text{SO}_2\text{Pb}$, and not $(\text{C}_2\text{H}_3\text{SO}_2)_2\text{Pb}$.

W. C. W.

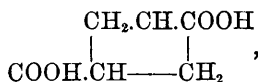
Purification of Carbon Bisulphide. By E. ALLARY (*Bull. Soc. Chim.* [2], **35**, 491—492).—In order to free carbon bisulphide from foetid impurities, the author agitates it with a concentrated solution of potassium permanganate until the permanence of a violet tint shows that the reducing action has ceased. The carbon bisulphide is then washed with water, separated by a funnel, and finally filtered; the pure ethereal-smelling liquid is then preserved from the action of light. The author finds that the usual method of distillation is in most cases practically useless.

V. H. V.

Occurrence of Malonic Acid in the Manufacture of Beet-sugar. By E. O. LIPPMANN (*Ber.*, **14**, 1183—1185).—Besides tricarballoylic and aconitic acids (this Journal, **38**, 36), the author has succeeded in obtaining malonic acid from the deposit of calcium salts formed in the vacuum pans in beet-sugar manufacture. The identity of the acid thus obtained is shown by its analysis and its melting point, viz., 134° , also by the properties and analyses of the barium,

($C_3H_2BaO_4 + 2H_2O$), and of the calcium ($4(C_3H_2CaO_4) + 7H_2O$) salt. P. P. B.

Homo-itaconic Acid. By M. KRESTOWNIKOFF (*Bull. Soc. Chim.* [2], 35, 558).—By the action of sodium ethylate on ethyl chloropropionate, the author has obtained, among other products, the ethyl salt of homo-itaconic acid, which by saponification with hydrochloric acid, gives the corresponding acid, $C_6H_8O_4$. This crystallises in prisms (m. p. $170-171^\circ$) soluble in warm water and alcohol, sparingly soluble in ether. Several metallic and ethereal salts were obtained. In like manner, by the action of sodium methylate on ethyl chloropropionate, the same acid is formed. Homo-itaconic acid differs from the acids of the fumaric series by not being acted on by hydrobromic or hydriodic acid, bromine, or sodium-amalgam. In order to explain these differences of behaviour of homo-itaconic and the isomeric muconic acids, the author assigns to the former the structural formula—



and proposes to name it provisionally symmetrical tetrylene dicarboxylic acid. By the action of an alcoholate on ethyl bromobutyrate an acid, $C_8H_{12}O_4$, is formed, which must be regarded as a homologue of homo-itaconic acid. V. H. V.

Derivatives of Pyromucic Acid. By C. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, 14, 1058—1059).—The authors confirm Wallach's description (*Ber.*, 14, 751) of the properties of pyromucamide (m. p. 142° , and not 132° as stated in the text-books) and furfuronitril (b. p. 147° under 757.8 mm. pressure). On boiling with potassium hydroxide, furfuronitril is converted into ammonia and pyromucic acid, and on treatment with zinc and sulphuric acid a small quantity of *furfurylamine*, $C_4H_3OCH_2NH_2$, was obtained. This compound is a colourless liquid, soluble in water, and smelling like conine.

W. C. W.

Action of Bromine on Uramil. By E. MULDER (*Ber.*, 14, 1060—1061).—Monobromamidobarbituric acid appears to be formed when uramil is heated at 85° in sealed tubes with six times its weight of bromine. The excess of bromine is removed from the product by means of a current of carbonic anhydride. The bromine in the acid could not be replaced by cyanogen.

W. C. W.

Optical Rotatory Power of Asparagine and Aspartic Acid in Different Solvents. By A. BECKER (*Ber.*, 14, 1028—1041).—One part of anhydrous asparagine requires for solution 82 parts of water at 10° and 47 at 20° . The specific rotation of this solution is -5.42 . An alkaline solution of asparagine gradually diminishes in volume and increases in density when left to itself; e.g., a solution which when freshly prepared had a sp. gr. of 1.1166 at 20° had, after the lapse of five days, the sp. gr. 1.1251. The rotatory power of

asparagine is increased by the addition of soda, decreased by acetic acid, and inverted by sulphuric or hydrochloric acid.

Asparagine, $C_4H_8N_2O_3$.	H ₂ O.		Specific rotation [α] _D .
1	63.8	1.0 mol. NaHO	— 8.64°
1	59.3	3.0 „ „	— 6.35
1	300.0	1.0 „ HCl.	+ 26.42
1	300.0	2.0 „ „	+ 31.52
1	300.0	5.0 „ „	+ 32.28
1	300.0	20.0 „ „	+ 34.26
1	300.0	0.5 „ H ₂ SO ₄	+ 23.05
1	300.0	1.0 „ „	+ 29.54
1	300.0	10.0 „ „	+ 35.45
1	300.0	1.0 „ C ₂ H ₄ O ₂	— 3.49
1	300.0	5.0 „ „	— 1.45
1	300.0	10.0 „ „	0
1	300.0	15.0 „ „	+ 1.11
1	300.0	20.0 „ „	+ 2.63

An aqueous solution of aspartic acid is feebly lævogyratory, the optical power is increased by the addition of soda or ammonia, diminished by acetic and inverted by the addition of sulphuric and hydrochloric acids.

Aspartic acid. $C_4H_7NO_4$.	H ₂ O.		Specific rotation [α] _D .
1	285.4	1.0 mol. NaHO	— 9.07°
1	276.5	5.0 „ „	— 9.04
1	302.0	1.0 „ NH ₃	— 9.17
1	302.0	5.0 „ „	— 9.61
1	302.0	20.2 „ „	— 12.05
1	203.4	0.10 „ HCl	— 0.56
1	238.7	0.12 „ „	0
1	256.2	0.13 „ „	+ 0.35
1	360.5	0.55 „ „	+ 14.87
1	64.4	1.0 „ „	+ 30.04
1	60.4	3.0 „ „	+ 33.96
1	311.0	25.0 „ „	+ 33.93
1	302.0	0.5 „ H ₂ SO ₄	+ 21.80
1	302.0	1.0 „ „	+ 28.83
1	302.0	5.0 „ „	+ 32.03
1	302.0	10.0 „ „	+ 33.50
1	285.0	1.0 „ C ₂ H ₄ O ₂	— 3.16
1	285.0	2.0 „ „	— 1.07
1	285.0	4.0 „ „	— 0.14
1	285.0	5.0 „ „	+ 0.14
1	285.0	10.0 „ „	+ 1.72

W. C. W.

Phosphoplatinic Compounds. By E. POMEY (*Compt. rend.*, **92**, 794 — 795). — In order, if possible, to obtain the compound, $P(C_2H_4Cl)_3.PtCl_4$, by substitution of Cl_3 for $3HO$ in Schützenberger's

phosphoplatinous ether, $P(C_2H_5O)_3.PtCl_2$, 16 grams of phosphorus pentachloride and 11 grams of the phosphoplatinous ether, both carefully dried, were mixed in a flask and heated in an oil-bath. At 40° , the mixture fused to a deep red liquid, which entered into ebullition, giving off monochlorethane. The substance in the flask gradually solidified to a brown mass. This was boiled with phosphorus trichloride, and the solution left to cool, when it deposited yellow crystals of the compound $PCl_3.PtCl_2$. The reaction may be represented by the equation $P(EtO)_3.PtCl_2 + 3PCl_5 = PCl_3.PtCl_2 + 3EtCl + 3POCl_3$.

When a solution of phosphoplatinous ether in carbon tetrachloride is mixed with a solution of bromine in the same liquid, a red crystalline precipitate, of the composition $P(EtO)_3.PtCl_2.Br_2$, is thrown down. The corresponding chlorine-compound may be obtained by substituting a saturated solution of chlorine for that of bromine. Both bodies are extremely hygroscopic, and are readily decomposed by atmospheric moisture. If bromine-water is added to a similar solution of phosphoplatinic ether, $P(EtO)_3.PtCl_2$, until the bromine is no longer absorbed, a deep red crystalline substance, of the composition $[P(EtO)_3]_2.PtCl_2.Br_2$, soluble in alcohol, is obtained. Phosphoplatinic ether also absorbs chlorine, but the composition of the body formed has not yet been determined.

C. H. B.

Parachlorobenzyl Compounds. By C. L. JACKSON and A. W. FIELD (*Ann. Chem. J.*, **2**, 85—96).—The *chloride*, $C_6H_4Cl.CH_2Cl$, prepared by direct chlorination of pure parachlorotoluene, crystallises in white lustrous prisms or needles melting at 29° (this Journal, **36**, 62).

Parachlorobenzyl alcohol, $C_6H_4Cl.CH_2OH$, prepared by boiling the bromide, chloride, or acetate with water, crystallises from boiling water in beautiful pointed white ribbons, usually one or two inches long, having a brilliant pearly lustre and peculiar smell; it does not attack the mucous membranes. It sublimes very easily in white needles; evaporates slowly on exposure to the air, and distils in a current of steam; dissolves sparingly in cold, much more readily in hot water, very easily in alcohol, ether, benzene, carbon sulphide, and glacial acetic acid. By chromic acid mixture it is oxidised to *p*-chlorobenzoic acid, melting at 233° .

Parachlorobenzyl cyanide, $C_6H_4Cl.CH_2.CN$, is formed by the action of potassium cyanide on *p*-chlorobenzyl bromide, and separates, on addition of water to the product, as a yellow oil which shows but little tendency to solidify: indeed it was only after standing in an open watch-glass for three or more weeks, and being then put into a mixture of ice and salt, that it deposited a small quantity of colourless prisms melting at 29° ; it is easily soluble in alcohol and ether, and remains, on evaporation of the solvent, as an oil which crystallises when stirred. The yellow oil appears to be identical in composition with the crystals, and, like the latter, is converted by heating with hydrochloric acid at 100° in a sealed tube into:

Parachloralphenol, $C_6H_4Cl.CH_2.COOH$. This acid may also be prepared by boiling the cyanide with dilute sulphuric acid in a flask with reversed condenser. When purified by solution in ammonia,

precipitation with sulphuric acid, and recrystallisation from boiling water, it forms white needles, sometimes thick and pointed. It has a pleasant odour, melts at $103.5\text{--}104^\circ$, sublimes easily in small plates, and may be distilled, though not quickly, in a current of steam; is somewhat soluble in cold, much more freely in hot water; freely in alcohol, ether, benzene, carbon sulphide, and glacial acetic acid. Aqueous ammonia dissolves it readily, but the resulting salt is decomposed, partly at least on evaporation, the acid being set free. The silver salt, $\text{C}_6\text{H}_5\text{ClO}_3\text{Ag}$, is a white curdy precipitate consisting of clumps of microscopic needles, which blacken rapidly in sunshine, very slowly in diffused daylight; it is very slightly soluble in boiling water, almost insoluble in cold water, freely soluble in dilute nitric acid and aqueous ammonia. The solution of the acid in ammonia, freed from excess of ammonia by evaporation, gives a precipitate of bluish-green flocks with cupric sulphate, yellowish-brown with ferric sulphate, white with lead acetate and mercurous nitrate.

Parachlorobenzyl thiocyanate, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{SCN}$, was prepared by boiling the bromide with alcoholic potassium thiocyanate, and purified by freezing with snow and salt, extracting the oil with filter-paper, and recrystallisation from alcohol in a freezing mixture. It forms white flattened needles often more than an inch long; has a strong disagreeable smell; melts at 17° ; does not distil with steam, but seems to be slowly decomposed by it; mixes with ether, benzene, carbon sulphide, and glacial acetic acid, but not with water.

Parachlorobenzylamines.—These compounds were discovered by Berlin (*Annalen*, **151**, 137), who obtained them by heating *p*-chlorobenzyl chloride with alcoholic ammonia in a steam-bath for a week. They may, however, be more readily prepared from the corresponding bromide, on which alcoholic ammonia acts very quickly, even at ordinary temperatures. The product obtained in this manner, or by heating the material together in a sealed tube at 100° , consists of crystals either of the hydrobromide of tri-parachlorobenzylamine, or of the base itself, and of an alcoholic solution which when filtered and evaporated on a steam-bath, yields ammonium bromide, together with the hydrobromides of di- and mono-*p*-chlorobenzylamine and some free trichlorobenzylamine. This residue, after washing with water to remove the hydrobromides of ammonia and the primary amine, was repeatedly crystallised from hot alcohol till it was separated into slightly soluble scales of di-*p*-chlorobenzylamine hydrobromide and needles of the free tertiary amine readily soluble in boiling alcohol.

Mono-p-chlorobenzylamine, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{NH}_2$ [$\text{Cl} : \text{CH}_2\text{NH}_2 = 1 : 4$]. This base, precipitated by caustic soda from the aqueous solution of its hydrobromide and distilled with steam, is a colourless oil nearly if not quite insoluble in water, but soluble in ether; on exposure to the air it is very quickly converted into a white soluble crystalline carbonate which crystallises from water in white plates, from alcohol in needles; melts at $114\text{--}115^\circ$; dissolves slowly in cold, quickly and freely in hot water and alcohol; and is decomposed by caustic alkalis, with separation of the base. The *hydrochloride* crystallises in long narrow white plates soluble in water and in alcohol, sparingly soluble in

glacial acetic acid, almost insoluble in ether, benzene, and carbon disulphide; melts at 239—241°. The *platinochloride*,

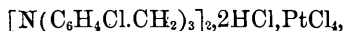


crystallises from water in round woolly groups of bright yellow branching needles or plates, soluble in alcohol. The *hydrobromide*, formed in the preparation of the amines, resembles the chloride in appearance and generally in solubility, though it is somewhat less soluble in water. It melts with decomposition between 225° and 230°.

Diparachlorobenzylamine, $\text{NH}(\text{C}_6\text{H}_4\text{Cl}.\text{CH}_2)_2$, separated from the hydrobromide by caustic soda, is an oil which solidifies on stirring, especially if touched with a crystal of the substance. It forms white radiating, bladed crystals, melting at 29°, insoluble in water, soluble in alcohol and glacial acetic acid, freely soluble in ether, benzene, and carbon sulphide. The *hydrochloride* is precipitated by hydrochloric acid from the alcoholic solution of the base, in microscopic, rhombic, and prismatic plates, apparently monoclinic, slightly soluble in water, alcohol, and glacial acetic acid, insoluble in ether and carbon sulphide, melting at 288°. The *platinochloride*, $[\text{NH}(\text{C}_6\text{H}_4\text{Cl}.\text{CH}_2)_2]_2, 2\text{HCl}, \text{PtCl}_4$, crystallises in pale yellow scales, slightly soluble in boiling water, almost insoluble in cold water and alcohol. The *hydrobromide*, obtained in the preparation of the amines, crystallises in white scales, very slightly soluble in water and in alcohol, insoluble in ether, easily decomposed by soda, melting with decomposition at 280—290°.

The salts just described are identical with those of the α -modification of Berlin's secondary chlorobenzylamine; his β , γ , and δ modifications appear to have consisted of mixtures of para- and ortho-compounds in varying proportions.

Triparachlorobenzylamine, $\text{N}(\text{C}_6\text{H}_4\text{Cl}.\text{CH}_2)_3$, crystallises from alcohol in bunches of white needles; from ether it separates as an oil which solidifies after some time in flattened prisms; when formed by the action of alcoholic ammonia on parachlorobenzyl bromide it separates in short thick well-formed rhombic crystals. It melts at 78·5°, is insoluble in water, very slightly soluble in cold, freely in hot alcohol, also in ether, benzene, and carbon sulphide, less soluble in glacial acetic acid. The *hydrochloride*, not quite pure, was obtained when an alcoholic solution of the base was heated with strong hydrochloric acid, and separated on spontaneous evaporation in spherical groups of radiate needles, melting at about 196°, soluble in ether, alcohol, and glacial acetic acid, slightly soluble in water, insoluble, or nearly so, in carbon sulphide and benzene. The *platinochloride*,



forms orange-coloured microscopic irregular plates, almost insoluble in water, alcohol, and ether. The *hydrobromide* crystallises in scales like those of the hydrobromide of the secondary amine, but less soluble in alcohol.

The following table exhibits a comparison of the melting points of the above-described compounds, as determined by Jackson and Field, with those of the same compounds according to former observers:—

	True melting point.	Old melting point.	Authority for old melting point.
Parachlorobenzyl chloride	29°	Liquid.	Beilstein u. Geitner.
" bromide	48·5°		
" alcohol	70·5	66°	Beilstein u. Kuhlberg.
" cyanide	29° (?)	Liquid.	Neuhof.
Parachlor- α -toluic acid	103·5—104°	60°	Neuhof.
		68	Radziszewski.
Parachlorobenzyl thiocyanate	17°		
Parachlorobenzylamine	Liquid.	Liquid.	Berlin.
" hydrochloride ..	239—241°	197°	"
" hydrobromide ..	225—230		
" carbonate	114—115		
Diparachlorobenzylamine	29°	Liquid.	"
" hydrochloride ..	288°	288—289°	"
" hydrobromide ..	280—290°	283—290	"
Triparachlorobenzylamine	78·5°	88—89	"
" hydrochloride ..	196° (?)	170—175	"

H. W.

Parachlorobenzyl Compounds. By C. L. JACKSON and J. F. WHITE (*Amer. Chem. J.*, **2**, 158—172).—1. *Parachlorobenzylsulphonic acid*, $C_6H_4Cl.CH_2.SO_3H$. The sodium salt of this acid was prepared by boiling a solution of normal sodium sulphite (1 mol.) with pure parachlorobenzyl bromide (1 mol.) in a return-cooler till the smell of the bromide was no longer perceptible. It crystallises from alcohol in pearly scales, from water in large flat colourless triclinic crystals. The *potassium salt*, prepared from the barium salt by double decomposition, resembles the sodium salt in appearance, but is much more soluble in alcohol. The *barium salt*, obtained by adding barium chloride to the solution of the sodium salt, or better by boiling the free acid with barium carbonate, crystallises from water in radiate bunches of needles moderately soluble in water, and having the composition—



The *calcium salt* $(C_6H_4ClSO_3)_2Ca + 7H_2O$, crystallises in rhombic plates, very much like flattened cubes, gives up 5 mol. water in a vacuum, the rest at 160°. The *copper salt* $(C_6H_4ClSO_3)_2Cu + 2H_2O$, is readily soluble in water, and crystallises in tufts of pale green needles. The *normal lead salt* $(C_6H_4ClSO_3)_2Pb + H_2O$, crystallises in long white needles, grouped in sheaves or stars, and is not very soluble in water.

The *hydrogen salt*, or *free acid*, prepared from the purified lead salt by decomposition with hydrogen sulphide, crystallises on evaporating its solution to a syrup, first over the water-bath, then at a lower temperature, and finally in a vacuum, in square plates, which soon turn yellow, and give off white fumes smelling of hydrochloric acid and benzaldehyde. These crystals melt with decomposition at 108°.

The *chloride*, $C_6H_4Cl.CH_2.SO_2Cl$, is obtained by acting on the dry

sodium salt with phosphorus pentachloride, and treating the product with water, as a heavy oil which soon solidifies, and may be purified by crystallisation from ether. It then forms flattened crystals often arranged in pennate groups. It has an aromatic odour, melts at 85.5° , is insoluble in water, dissolves in ether and alcohol, but seems to be decomposed by the latter.

Parachlorobenzyl sulphide, $(C_6H_4Cl.CH_2)_2S$, was obtained by heating parachlorobenzyl chloride or bromide with an alcoholic solution of sodium sulphide, and precipitating the product with water, in the form of a heavy oil, the solution of which in hot alcohol yielded a purer oil, which solidified on standing over night, and was further purified by crystallisation from hot alcohol. It forms thick nearly inodorous needles melting at 42° ; cannot be sublimed without decomposition; is nearly insoluble in water; dissolves in cold, more freely in hot alcohol, easily in ether, carbon sulphide, benzene, and glacial acetic acid.

Diparachlorobenzylsulphone, $(C_6H_4Cl.CH_2)_2SO_2$, prepared by gradual addition of chromic anhydride to the preceding compound, both being dissolved in glacial acetic acid, or by the oxidising action of the air on parachlorobenzyl sulphide, crystallises in very small needles melting at 165° , not sublimable without decomposition, nearly insoluble in water, readily soluble in alcohol, carbon sulphide, glacial acetic acid, and ligroin. The isomeride melting at 149° , which Vogt and Henninger obtained by the action of chlorobenzyl chloride on potassium sulphite, was probably the corresponding orthochlorobenzylsulphone.

Parachlorobenzyl-mercaptan, $C_6H_4Cl.CH_2.SH$, is formed on mixing the alcoholic solutions of parachlorobenzyl bromide and potassium hydrosulphide, the mixture becoming hot, and the action being completed in about half an hour without the aid of external heat. The product treated with water deposits a dark-coloured oil, which may be purified by distillation with steam, freezing in a mixture of ice and salt, and recrystallisation from alcohol with the aid of a freezing mixture.

Parachlorobenzyl-mercaptan is, at ordinary temperatures, a colourless oil, but when cooled by a mixture of ice and salt, it solidifies in white crystals which melt at $19-20^{\circ}$. It distils with steam, and mixes readily with alcohol, ether, benzene, and carbon sulphide, but not with water. Yellow mercuric oxide attacks it with great energy, converting it into the corresponding mercaptide $(C_6H_4Cl.CH_2.S)_2Hg$, which, when purified by repeated recrystallisation from boiling alcohol, forms light white scentless needles, apparently having no fixed melting point, but turning red or black, and shrinking to about half their original bulk when heated to about 160° . This mercaptide is insoluble in water, very slightly soluble in ether, benzene, carbon sulphide, glacial acetic acid, and cold alcohol, somewhat more freely in hot alcohol; decomposed by hydrogen sulphide into mercuric sulphide and the mercaptan.

Parachlorobenzyl Disulphide $(C_6H_4Cl.CH_2)_2S_2$.—Prepared: 1. By prolonged boiling of parachlorobenzyl bromide with alcoholic potassium hydrosulphide. 2. By treating parachlorobenzyl-mercaptan with the calculated quantity of bromine dissolved in ether: $2C_6H_4ClSH +$

$\text{Br}_2 = 2\text{HBr} + (\text{C}_7\text{H}_6\text{Cl})_2\text{S}_2$. With a large excess of bromine, an aromatic oil is produced, which has not yet been examined. 3. By heating parachlorobenzyl bromide with alcoholic sodium disulphide. It forms white flattened needles smelling somewhat like mercaptan; melts at 59° ; is insoluble in water, readily soluble in alcohol, glacial acetic acid and ligroin, very soluble in ether, benzene, and carbon sulphide; not acted upon by mercuric oxide or chloride; converted by nascent hydrogen (zinc and dilute sulphuric acid) into the corresponding mercaptan.

The same compound appears to have been obtained in an impure state by Beilstein (*Annalen*, **116**, 336) and by Neuhoﬀ (*ibid.*, **147**, 339), both of whom, however, regarded it as the mercaptan, and found its melting point to be between 84° and 85° .

Parachlorobenzyl disulphodioxide $(\text{C}_6\text{H}_4\text{Cl}.\text{CH}_2)_2\text{S}_2\text{O}_2$, is formed on treating the disulphide with the calculated quantity of chromic anhydride, both dissolved in glacial acetic acid, and is deposited on addition of water, as an oil which solidifies on standing in the cold, and may be purified by crystallisation from alcohol. It is a waxy solid, becoming crystalline after some time, and melting at 120° ; insoluble in water, easily soluble in alcohol, ether, benzene, carbon sulphide, and glacial acetic acid.

Ethylie parachlorobenzylate, prepared by boiling the bromide with alcoholic sodium hydroxide, is a colourless liquid, distilling at 215 — 225° , and not solidifying at -12° .

The following table exhibits a comparison of the melting points of these compounds prepared as above described, with those of the same bodies obtained by former observers from more or less impure materials :—

Formula.	True melting point.	Former melting point.	Authority for former melting point.
$\text{C}_7\text{H}_6\text{Cl}.\text{SO}_2\text{Cl}$	85.5°		
$(\text{C}_7\text{H}_6\text{Cl})_2\text{S}$	42°	Oil.	Pauly.
$(\text{C}_7\text{H}_6\text{Cl})_2\text{SO}_2$	165°	167°	Vogt u. Henninger.
$\text{C}_7\text{H}_6\text{Cl}.\text{SH}$	19°	$\begin{cases} 77-78^\circ \\ 84-85 \\ 84-85 \end{cases}$	Beilstein.
$(\text{C}_7\text{H}_6\text{Cl})_2\text{S}_2$	59°	See above.	Neuhoﬀ.
$(\text{C}_7\text{H}_6\text{Cl})_2\text{S}_2\text{O}_2$	120°		
$\text{C}_7\text{H}_6\text{Cl}.\text{O}.\text{C}_2\text{H}_5$	Oil.	$\begin{cases} \text{Oil.} \\ \text{Oil.} \end{cases}$	Naquet. Neuhoﬀ.

H. W.

Crystallisation of α - and β -Dinitroparaxylenes. By P. JANNASCH and C. SRÜNKEL (*Ber.*, **14**, 1146—1150).—The authors find that by crystallising a mixture of these isomerides from glacial acetic acid, crystals are obtained of well defined form, melting at 99 — 99.5° . These crystals retain their form and melting point when crystallised from glacial acetic acid, but when crystallised from alcohol they are separated into the two isomerides, melting at 123.5° and 93° respectively.

The authors are inclined to regard the crystals obtained from glacial acetic acid as a definite compound of equal molecules of each of the above isomerides.
P. P. B.

Occurrence of an Aromatic Hydrocarbon, $C_{11}H_{16}$, in Rosin Oil. By W. KELBE (*Ber.*, **14**, 1240—1241).—The author has succeeded in isolating the hydrocarbon $C_{11}H_{16}$ contained in the portion of rosin oil which boils between 190° and 200° , by the same process by which he obtained metaisocymene from the lower boiling fraction of rosin oil (*Ber.*, **13**, 1161; this Journal, Abstr., 1880, 878), viz., by digesting with strong sulphuric acid at 100° . The lead salt of the sulphonic acid $(C_{11}H_{15}SO_3)_2Pb + 3H_2O$, crystallises in plates, which are much more soluble in hot than in cold water. The sulphamide forms needle-shaped crystals melting at 64° .

The hydrocarbon, $C_{11}H_{16}$, prepared by heating the lead salt with hydrochloric acid, is a colourless, highly refractive liquid (b. p. $186-188^\circ$). Since it yields isophthalic acid on oxidation with chromic mixture, it must be either methylbutyl-benzene or ethylpropyl-benzene.
W. C. W.

Diazobenzene Nitrate. By BERTHELOT and VIEILLE (*Compt. rend.*, **92**, 1074—1079).—Diazobenzene nitrate may be kept in dry air in the dark for several months without undergoing alteration, but if exposed to the light it gradually decomposes, becoming rose-coloured. This decomposition takes place much more rapidly in a moist atmosphere. The compound gives off an odour of phenol, and finally swells up and becomes black, giving off gas. Diazobenzene nitrate is more sensitive to percussion than mercury fulminate, and explodes when heated above 90° , whereas the fulminate does not explode until the temperature reaches 195° . When heated in small portions it decomposes gradually, without detonation, even below 90° . Density of diazobenzene nitrate = 1.37; heat of combustion at constant volume = + 783.9 cal.; at constant pressure, 782.9 cal.; heat of formation = - 47.4 cal. The detonation of one molecule (167 grams) develops heat = + 114.8 cal., and produces 136.6 litres of gas (corr. vol.); the detonation of 1 kilo. develops therefore + 687.7 cal., and produces 817.8 litres of gas. The percentage composition of the gas produced is as follows:—

HCN.	CO.	CH ₄ .	H.	N.
3.2	48.65	2.15	27.7	18.3 = 100

The whole of the oxygen combines with carbon to form carbonic oxide, and no water is formed. Three-fourths only of the nitrogen is set free, one-fifth forms hydrocyanic acid, and the rest remains in the solid residue, partly as ammonia, partly in the form of a special nitrogen compound. Exactly half the carbon is converted into carbonic oxide. The solid residue is a voluminous, impalpable powder, resembling charcoal, with an ammoniacal odour. It has approximately the composition C_6HN , and contains about 0.011 gram ammonia per gram of explosive: the gaseous products contain 0.0004 gram. The principal decomposition may be represented by the equation

$C_6H_4.N_2.HNO_3 = 3CO + 3C + H_2 + N_2$. This reaction would develop heat = + 201.6 cal., whereas the amount actually developed is + 114.8 cal., from which it follows that the formation of the secondary products has absorbed - 86.8 cal., an absorption mainly due to the formation of the azotised carbon, the heat developed by the formation of the ammonia and methane being almost equal to that absorbed by the production of the hydrocyanic acid. This result agrees with the general observation that hydrocarbons containing but little hydrogen, and carbonaceous bodies retain a considerable portion of the energy of their complex generators, a fact which explains the endothermic formation of certain compounds when organic bodies are decomposed by heat.

The following table gives the pressures developed by the explosion of diazobenzene nitrate under certain conditions, compared with those developed by mercury fulminate under similar conditions:—

Density.	Weight of charge.	Pressure per sq. cm.	Pressure with mercury fulminate.
0.1	2.37 grams.	990 kilos.	480 kilos.
0.2	4.74 „	2317 „	1730 „
0.3	7.11 „	4587 „	2700 „

Diazobenzene nitrate gives higher pressures than mercury fulminate for the same density of charging, but on the other hand, when the fulminate is detonated in a space which it exactly fills, it develops a pressure of 44,000 kilos. per square cm., whereas diazobenzene nitrate under the same conditions gives a pressure of only 15,000 kilos., a difference due to the much higher density of the fulminate.

C. H. B.

Action of Acetamide on Phenylcyanamide. By F. BERGER (*Ber.*, 14, 1256—1258).—With the view of preparing phenylacetic guanidine, a mixture of acetamide and phenylcyanamide in their molecular proportions was heated for two to three hours in a flask provided with an upright condenser. No phenylacetic guanidine was formed, but three compounds were obtained, one of which was insoluble in alcohol and most of the usual solvents. To separate these bodies, the alcoholic extract of the crude product was mixed with strong hydrochloric acid; the precipitated hydrochlorides collected on a filter and recrystallised from alcohol. The hydrochloride, $C_{18}H_{17}N_5.HCl$, is deposited in needles which melt between 256° and 264° . The free base, $C_{18}H_{17}N_5$, also crystallises in needles (m. p. 233°) soluble in alcohol.

The mother-liquor from the compound $C_{18}H_{17}N_5.HCl$ contains a more soluble hydrochloride, which was not obtained in sufficient quantity for analysis.

That portion of the original crude product which is insoluble in alcohol, dissolves in strong hydrochloric acid. It is precipitated from the acid liquid on the addition of water. From an alcoholic solution containing hydrochloric acid, it is deposited in flattened needles which do not melt at 292° . The composition of this substance appears to be very complicated.

W. C. W.

Action of Hydrochloric Acid Gas on Thiocarbimides and Thiocyanic Ethers in presence of Absolute Alcohol. By A. PINNER and W. SCHAUMANN (*Ber.*, **14**, 1082—1083).—A mixture of absolute alcohol and phenyl thiocarbimide saturated with gaseous hydrochloric acid slowly deposits crystals of aniline hydrochloride, $\text{PhNCS} + \text{H}_2\text{O} = \text{PhNH}_2 + \text{COS}$.

From a mixture of ethyl thiocyanate and alcohol saturated with hydrochloric acid, crystals of isothiurethane, $\text{NH}_2\text{CO.SEt}$ (m. p. 102°), are deposited. This compound splits up into mercaptan and cyanuric acid when heated in sealed tubes at 150° . W. C. W.

Compounds of Mono- and Di-basic Acids with Phenols. (Parts II and III). By M. NENCKI and N. SIEBER (*J. pr. Chem.*, **23**, 537—550).—Part II. The authors have previously described a dioxyacetophenone, which is obtained by the action of glacial acetic acid and zinc chloride on resorcinol. The name *resacetophenone* is now proposed for this ketone. On reducing the nitroresacetophenone previously described with tin and hydrochloric acid, it yields the corresponding *amido*-derivative, $\text{C}_6\text{H}_2(\text{OH})_2\text{Ac.NH}_2(\text{HCl})$, its hydrochloride readily crystallising in brilliant white prisms.

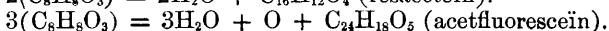
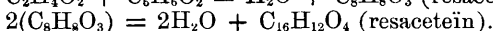
Gallacetophenone is obtained on heating pyrogallol with glacial acetic acid and zinc chloride at 145° . Its potassium salt crystallises in needles, $\text{C}_6\text{H}_3\text{O}_4 + \text{KOH}$, rapidly becoming brown on exposure to the air.

When resorcinol is heated with acetic acid and zinc chloride for some time, to the boiling point of the mixture, and the product is poured into water, a resinous substance separates, exhibiting a green metallic lustre. This is dissolved in hot alcohol, the solution acidified and diluted, and after separation of precipitated resin, neutralised with ammonia, when it yields an orange-coloured precipitate, readily separable by alcohol into acetofluoresceïn and resaceteïn.

Resaceteïn, $\text{C}_{16}\text{H}_{12}\text{O}_4$, although little soluble in alcohol, dissolves in aqueous ammonia, forming a pink solution, and from this shining red needles separate. It dissolves readily in dilute hydrochloric acid with yellow coloration, but is insoluble in strong hydrochloric acid. Its hydrochloride, $\text{C}_{16}\text{H}_{12}\text{O}_4.\text{HCl} + 2\text{H}_2\text{O}$, forms fine red prisms, losing their water of crystallisation at 110° . The sulphate crystallises in yellow needles. Resaceteïn dissolves in alkalis, with production of a magnificent red coloration, but its ammoniacal solution is the only one that is at all permanent. Zinc-dust at once decolorises the latter, and the product of reduction can be precipitated by hydrochloric acid in yellow amorphous flocks. Bromine yields a red unstable substitution product; nitrous acid, a fairly permanent colouring matter, dyeing silk and wool reddish-brown.

Acetfluoresceïn, $\text{C}_{24}\text{H}_{18}\text{O}_5$, is easily soluble in alcohol and in alkalis, its solution in the latter exhibiting a fine green fluorescence. The hydrochloride and sulphate have been obtained.

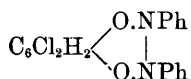
The formation of these bodies is explained by these equations:—



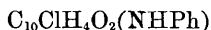
Part III. Quinol, when heated in a similar manner with acetic acid and zinc chloride yields *quinacetophenone*, $C_8H_8O_3$ (m. p. 202°), readily soluble in alcohol and in ether; it crystallises in yellowish needles, rapidly turning brown in the air. With acetic anhydride it yields a crystalline derivative. It strikes a fugitive blue coloration with ferric chloride, and reduces alkaline copper solution.

Resaurin, $C_{18}H_{14}O_6$, is produced by the action of resorcinol and zinc chloride on formic acid. It forms a brick-red amorphous and very hygroscopic powder, soluble in alcohol. In hot alkalis it dissolves with the production of a fine dark red colour. It is homologous with aurin, and is probably identical with the *diversorcinolketone* obtained by Claus and Andreæ from resorcinol and oxalic acid. O. H.

Action of Ammonia and Amines on Chloroquinones. By H. v. KNAPP (*Ber.*, **14**, 1233—1235).—The compounds which are produced by the action of ammonia or amines on trichloroquinone are regarded on the one hand by Kekulé and Hofmann (*Jahresb.*, 1863, 415) as quinone substitution products, and on the other by Wichelhaus (*Ber.*, **5**, 851, this Journal, 1873, 173) as quinol derivatives in which the hydrogen of the hydroxyl groups has been replaced by amine or ammonia residues. In order to ascertain the constitution of these bodies, the author has studied the action of ammonia, amiline, and ortho- and para-toluidine on trichloroquinone, tetrachloroquinone, trichlorotoluquinone, and dichloronaphthoquinone. The chief product of the reaction is an amidochloroquinone, but an amorphous substance, soluble also in alcohol, is also formed in considerable quantity. The behaviour of the amidated chloroquinones, on reduction with stannous chloride, testifies to the correctness of Hofmann's views of their constitution, *e.g.*, chloranilanilide yields the compound $C_6Cl_2(OH)_2(NHPh)_2$, and not dichloroquinol and aniline, showing that chloranilanilide has the formula $C_6Cl_2O_2(NHPh)_2$, and not



Dianilidochloroquinone $C_6ClHO_2(NHPh)_2$ (from aniline and trichloroquinone) and monochloronaphthoquinoneanilide,



(from aniline and dichloronaphthoquinone) also yield on reduction with stannous chloride colourless products which are converted back into the original compounds by oxidation. W. C. W.

Pyroguajacol. By H. WIESER (*Wien. Akad. Ber.* [2 Abth.], 464—478).—Pyroguajacol is the oily body which passes over last when guaiacum is submitted to dry distillation. According to the author it consists of C_6H_6O (or more probably $C_{18}H_{18}O_3$), whilst Ebermayer states that it consists of C_7H_7O , and Hlasiwetz gives the formula as $C_{19}H_{22}O_3$.

It crystallises in tolerably large rhombic plates (m. p. 180.5° , un-

corr.), sparingly soluble in boiling water, alcohol, and ether. The alcoholic solution gives no reaction with ferric chloride. It dissolves in sulphuric acid with a dark blue colour, and on adding water a dark blue flocculent precipitate is thrown down, whilst the liquid above appears colourless.

When sublimed, pyroguajacol forms small masses of needles mixed with plates, but when it is heated very slowly, distinct pointed needles are obtained. Sublimed in hydrogen it forms tolerably large plates.

Acetylpyroguajacol, $C_{18}H_{16}O_3\bar{A}c_2$, formed by heating pyroguajacol with acetic chloride in a glass tube, consists of colourless needles (m. p. 122°).

Dibenzoyl-pyroguajacol, $C_{18}H_{16}O_3\bar{B}z_2$, is formed by acting on pyroguajacol with benzoic chloride. It crystallises imperfectly, and melts at 179° .

Tribromopyroguajacol, obtained by dissolving pyroguajacol in acetic acid and adding bromine drop by drop, forms yellowish-red needles (m. p. 172°), which are sparingly soluble in alcohol.

When pyroguajacol is distilled over zinc-dust, brilliant plates (m. p. $100-101^\circ$) are obtained, which exhibit a faint blue fluorescence, and form a brownish-yellow prismatic compound with picric acid. The author proposes to call this new hydrocarbon ($C_{12}H_{12}$) *guajene*.

On oxidising an acetic acid solution of guajene with nitric acid, it yields a new body ($C_{12}H_{10}O_2$) of an orange colour, which may be regarded as guajaquinone.

When pyroguajacol is heated with potassium hydroxide, a body is formed which, when treated with dilute sulphuric acid, yields greyish-white flocculent masses (m. p. 202°), easily soluble in alcohol and ether. These probably consist of $C_{12}H_{12}O_2$.

From the above facts the rational constitution of pyroguajacol would seem to be $HO.C_{12}H_{10}.O.C_6H_5.OH$.
G. T. A.

Action of Nitric Acid on Deoxybenzoïn. By A. BORODIN (*Bull. Soc. Chim.* [2], 35, 560).—By the action of nitric acid on deoxybenzoïn, besides two isomeric dinitro-derivatives already described, the author has obtained a third, crystallising in yellow needles (m. p. 154°). He proposes to study the products of oxidation and reduction of these isomerides.
V. H. V.

Benzpinacone and Benzpinacolin. By A. ZAGOUMENNY (*Bull. Soc. Chim.* [2], 35, 560).—A continuation of the author's former researches. Benzpinacone (m. p. 168°), when crystallised from boiling alcohol is gradually altered, and the increased percentage of carbon shown by analysis points to a loss of water and the transformation of benzpinacone into benzpinacolin. A similar change has been observed by Thörner and Zincke (Abstracts, 1880, 114—117), which led them to believe in the existence of a isomeride, α -benzpinacolone. The author considers that the difference of melting point of benzpinacone found by Linnemann ($170-180^\circ$) and by Thörner and Zincke ($185-186^\circ$), may be attributed to the same cause.
V. H. V.

Action of Bromine on Orthonitrobenzoic Acid. By A. CLAUS and A. LADE (*Ber.*, **14**, 1168—1171).—Bromine reacts with orthonitrobenzoic acid and water in sealed tubes, at 250—260°, and amongst the products are tetrabromobenzene (m. p. 160°) and two isomeric dibromobenzoic acids. The di-bromobenzoic acids are separated from tetrabromobenzene by conversion into their barium salts, and from unaltered nitrobenzoic acid by repeated crystallisation of these salts. The acid prepared from the barium salt so obtained melts at 135°, but by repeated extraction with hot water it is separated into the two following dibromobenzoic acids, melting at 148° and 153° respectively.

The *ortho-allometa-dibromobenzoic acid* [1 : 2 : 5], m. p. 153°, which is the least soluble in water, forms a barium salt, $\text{Ba}(\text{C}_7\text{H}_3\text{Br}_2\text{O}_2)_2 + 2\frac{1}{2}\text{H}_2\text{O}$. This acid the authors regard as identical with that described by Hübner and Lemrie (*Ber.*, **10**, 1074), and Richter (*Ber.*, **7**, 145; **8**, 1418), Neville and Winther (this Journal, Trans., **37**, 435), and by Smith (*Ber.*, **10**, 1076).

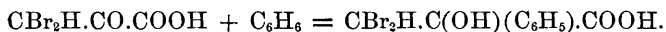
The *ortho-metadibromobenzoic acid* [1 : 2 : 3], m. p. 148°, is the acid most soluble in water, and identical with that obtained by Neville and Winther (*loc. cit.*) from meta-orthodibromotoluene. This acid is formed in the largest quantity in the above reaction. The following salts are described:—The *barium salt*, $\text{Ba}(\text{C}_7\text{H}_3\text{Br}_2\text{O}_2)_2 + 3\text{H}_2\text{O}$, is sparingly soluble in cold, but more so in hot water, and crystallises in colourless warty aggregations of needles. The *calcium salt*, $\text{Ca}(\text{C}_7\text{H}_3\text{Br}_2\text{O}_2)_2 + 2\text{H}_2\text{O}$, crystallises in small white needles, united in stellate groups, it is easily soluble in hot water. The *potassium salt*, $\text{KC}_7\text{H}_3\text{Br}_2\text{O}_2 + \text{H}_2\text{O}$, is very easily soluble in water, from which it crystallises in beautiful needles.

P. P. B.

Nitration of Benzoyl Cyanide and its Derivatives. By C. T. THOMPSON (*Ber.*, **14**, 1185—1188).—Benzoyl cyanide is nitrated by mixing it with sulphuric acid, cooling well and adding small quantities of nitre from time to time; the mixture is then poured into cold water. The chief product of nitration is metanitrobenzoic acid; a small quantity of liquid is also obtained, which, when boiled with concentrated hydrochloric acid, yields metanitrophenylglyoxylamide (this Journal, **38**, 253). This latter compound is obtained in larger quantities by the direct nitration of phenylglyoxylamide, some metanitrobenzoic acid being formed at the same time, and a small quantity of a substance, the exact nature of which has not been determined. Phenylglyoxylic acid is decomposed by sulphuric acid, and potassium nitrate even below -10°.

P. P. B.

Introduction of Aromatic Hydrocarbons into Ketonic and Aldehydic Acids. By C. BÖTTINGER (*Ber.*, **14**, 1235—1240).—Benzene combines directly with dibromopyrroacemic acid, forming dibromatrolactic acid,



In order to bring about this act of combination, dibromopyrroacemic acid is dropped in small quantities at a time into 20 times its weight

of well cooled strong sulphuric acid. Benzene is then added, and the mixture stirred until a clear solution is obtained. After an interval of four hours, crystals begin to separate out, and on pouring the thick liquid into cold water, dibromatrolactic acid is precipitated. A further yield of the acid may be obtained by extracting the filtrate with ether. The acid is purified by recrystallisation from chloroform. From this solvent it is deposited in glistening needles (m. p. 167°), and crystallises from a solution in carbon bisulphide or benzene in four-sided plates.

From its solution in alkalis it is precipitated unaltered by acids. It is decomposed by boiling with water, splitting up into carbonic anhydride, hydrobromic acid, and acetophenone bromide, C_6H_7BrO (m. p. 50°), described by Hunnius (*Ber.*, **10**, 2006, this Journal, Abstr., 1878, 147).

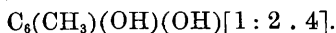
On reduction with sodium amalgam, a solution of dibromatrolactic acid is converted into atrolactic acid, and a small quantity of a syrupy acid, which slowly solidifies.

The author is studying the condensation-products of glyoxylic and mesoxalic acids with aromatic hydrocarbons. W. C. W.

A New Derivative of Gallic Acid and its use as an Indicator for the Estimation of Combined Carbonic Acid. By J. OSER and W. KALMANN (*Wien. Akad. Ber.*, **83** [ii], 161—167).—In a former communication (*Wien. Akad. Ber.*, **72** [ii]) on the action of potassium permanganate and sulphuric acid on gallic acid, one of the authors described the formation of an acid, $C_{14}H_{10}O_8$, which he called tetrahydroellagic acid. The authors by fusing this acid with potassium hydroxide until a sample taken out gives a greenish-yellow precipitate with sulphuric acid, have converted it into an isomeric acid. The new acid, $C_{14}H_{10}O_8$, crystallises from water in fine greenish-yellow microscopic needles with no water of crystallisation. It can be heated in a stream of hydrogen to 200° without undergoing any change; between 200° and 220° it begins to sublime; at 220 — 230° it becomes dark, and above this temperature is completely decomposed. It is soluble in hot water, alcohol, and ether, but only very sparingly in cold water. Its aqueous solution is coloured red-brown by ferric chloride, and olive-green by ferrous sulphate. Its alcoholic solution is rendered slightly turbid by an alcoholic solution of copper acetate, and with alcoholic lead acetate it gives a yellowish-green precipitate, which quickly turns dark brown. If sodium or potassium hydroxide is added to the acid suspended in water, at first there is only an olive-green solution, but as soon as the alkali is in excess the colour changes to carmine; this change is greatly accelerated by shaking with air. This solution has great tinctorial power; it is not altered by carbonic acid; but is turned yellow by the smallest excess of acid (dilute HCl and H_2SO_4); it is hence recommended as an indicator in the titration of sodium and potassium hydroxide, and as the red colour is also produced by calcium and magnesium carbonates, it can also be used in the estimation of the combined carbonic acid in water. Several analyses are given showing its efficiency. D. A. L.

α -Toluenedisulphonic Acid and its Derivatives. By C. FAHLBERG (*Amer. Chem. J.*, 1880, **2**, 181—198).—The author has already shown (this Journal, 1879, Abstr., 804) that tolueneparasulphochloride treated with concentrated or with fuming sulphuric acid, yields an α -toluenedisulphonic acid, identical with that which Blomstrand obtained by the action of fuming sulphuric acid at 160° on toluenemonosulphonic acid or one of its salts (*ibid.*, 1873, 505); and he now finds that the same disulphonic acid is produced by the action of fuming sulphuric acid at temperatures not exceeding 150° on tolueneorthosulphochloride; consequently the disulphonic acid must have the constitution $\text{CH}_3 : \text{SO}_3\text{H} : \text{SO}_3\text{H} = 1 : 2 : 4$.

By fusion with potassium hydroxide it yields salicylic acid, para-hydroxybenzoic acid, resorcinol, and isorcinol—

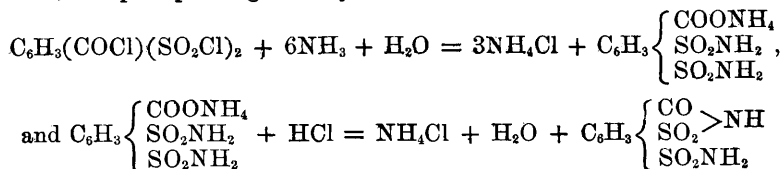


The corresponding *chloride*, $\text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_2\text{Cl})_2$, is obtained in nearly theoretical quantity by the action of PCl_5 on the pure potassium salt; when purified by washing with water and recrystallisation from ether, it melts at 52° .

The *disulphonamide*, $\text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_2\text{NH}_2)_2$ (m. p. 186 — 187°), is obtained by the action of aqueous, or better, of alcoholic ammonia on the dichloride. It is very soluble in excess of ammonia, and does not separate from the solution till that excess has been driven off.

Sulphaminebenzoic sulphinide,* $\text{C}_7\text{H}_6\text{N}_2\text{S}_2\text{O}_5 = \text{C}_6\text{H}_3 \begin{matrix} \text{CO} \\ \text{SO}_2 \\ \text{SO}_2\text{NH}_2 \end{matrix} \text{NH}$ (or

para-anhydrosulphaminebenzoic acid), is prepared by heating the disulphonamide with an aqueous solution of potassium permanganate, and separates, on addition of hydrochloric acid, as a colourless precipitate. It may also be prepared by treating the normal potassium salt of disulphobenzoic acid (*infra*) with phosphorus pentachloride, converting the resulting sulphochloride into the corresponding amide by the action of aqueous ammonia, evaporating the product to a small bulk, and precipitating with hydrochloric acid:—



Sulphaminebenzoic sulphinide crystallises from a saturated aqueous solution as a fine powder, and from a dilute solution in small rhombic plates. It dissolves sparingly in cold, more readily in hot water, and

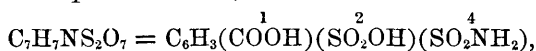
* The corresponding ortho-compound has been already described by Fahlberg u. Remsen (*Amer. Chem. J.*, **1**, 426; *Ber.*, **12**, 469; this Journal, 1879, Abstr., 628), who further propose the name "sulphinide" to designate compounds containing the group $\begin{matrix} \text{CO} \\ \text{SO}_2 \end{matrix} \text{NH}$; thus the compound $\text{C}_6\text{H}_4 \begin{matrix} \text{CO} \\ \text{SO}_2 \end{matrix} \text{NH}$, formerly called *anhydrosulphamine-benzoic acid* (though neither an acid nor an anhydride), is now to be called "benzoic sulphinide."

is almost insoluble in cold hydrochloric acid; but on boiling the solution with hydrochloric acid, the sulphinide is converted into sulphaminesulphobenzoic acid, $C_6H_3(SO_2NH_2)(SO_2OH)(COOH)$.

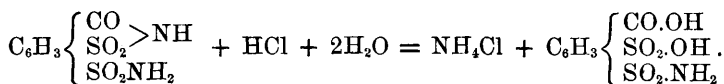
The sulphinide dissolves in alcohol and ether very easily, and without change, even in presence of hydrochloric acid. It melts with partial decomposition at 285° . It is not acted upon by phosphorus pentachloride, either at ordinary temperatures or when heated: hence it does not contain a hydroxyl-group.

Disulphaminebenzoic acid, $C_7H_8N_2S_2O_6 = C_6H_3(SO_2NH_2)_2COOH$. The salts of this acid are formed on neutralising the aqueous solution of sulphaminebenzoic sulphinide with carbonates. They are all very hygroscopic, and have not been obtained in crystalline form. Strong acids added to their solutions throw down, not the corresponding acids, but the sulphinide. The composition of the acid has been established by the analysis of the calcium salt, $(C_7H_7N_2S_2O_6)_2Ca$, which gave 6.80 and 7.00 per cent. C, the formula requiring 6.69, and from that of the ethylic ether, $C_6H_3(SO_2NH_2)_2COOC_2H_5$, which is prepared by the action of dry hydrogen chloride on a solution of the sulphinide in absolute alcohol; crystallises from water in long silky needles (melting at $198-200^\circ$); and gives by analysis 20.82 per cent. sulphur and 9.26 nitrogen, the formula requiring 20.78 S and 9.08 N.

Sulphamine-sulphobenzoic acid,



is produced by boiling the sulphinide with dilute hydrochloric acid, and separates on boiling down the solution to a very small bulk, in crystals which may be purified by recrystallisation from hydrochloric acid:—



The same acid is formed, as already mentioned, when the undried first precipitated sulphinide is recrystallised from boiling water.

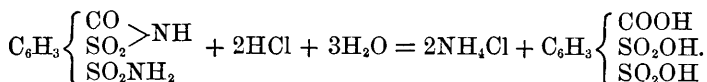
Sulphamine-sulphobenzoic acid is so easily soluble in water that it cannot be crystallised in aqueous solution, except over sulphuric acid. From hydrochloric acid, in which it is less soluble, it separates in large beautiful crystals, not hygroscopic, permanent in the air, and melting without decomposition at 165° . It is slightly soluble in alcohol, quite insoluble in ether.

The *monopotassic salt*, $C_6H_3(COOH)(SO_2OK)(SO_2NH_2)$, is obtained by treating the dipotassic salt with excess of hydrochloric acid, and evaporating the solution after the potassium chloride formed at the same time has crystallised out; it forms beautiful transparent crystals, apparently belonging to the rhombic system.

[1 : 2 : 4] *Disulphobenzoic acid*, $C_6H_3(COOH)(SO_3H)(SO_3H)$.—This acid, which was obtained by Hakanson (*Ber.*, 5, 1088) and afterwards by Blomstrand (*loc. cit.*) by oxidising α -toluenedisulphonic acid with chromic acid mixture, is also formed together with sulphobenzoic sulphinide by oxidation of [1 : 2 : 4] toluedisulphonamide with per-

manganate. When the mother-liquor of the sulphinide is evaporated to a small bulk, potassium chloride separates out, and on repeating the operation till no more of the salt is deposited, the last mother-liquor yields on evaporation a large quantity of dipotassic disulphobenzoate, $C_6H_3(COOH)(SO_3K)_2$, which separates from its aqueous solution in large rhombic crystals. It is more soluble in cold than in hot water, less soluble in cold hydrochloric acid than in water, not acted upon by alcohol or ether.

The same disulphobenzoic acid is formed together with ammonium chloride when sulphobenzoic sulphinide is heated in a sealed tube with hydrochloric acid—



On evaporating the resulting solution to dryness, heating the residue to 200° , to volatilise the ammonium chloride, and crystallising it from strong hydrochloric acid, the disulphobenzoic acid is obtained in large beautiful crystals, permanent in the air, melting above 285° , and solidifying on cooling to a transparent amorphous mass. It dissolves readily in water, but is insoluble in alcohol and ether.

[1 : 2 : 4] *Dihydroxybenzoic acid*, $C_6H_3(COOH)(OH)(OH)$.—This acid, discovered by Ascher (*Ber.*, **4**, 649; this Journal, 1871, 827), is, according to Blomstrand (*Ber.*, **5**, 1084; this Journal, 1873, 506), the only product obtained by fusing the corresponding disulphobenzoic acid with potassium hydroxide. Fahlberg, however, finds that this is true only when the temperature is kept below 250° ; but that by prolonged fusion at higher temperatures the dihydroxy-acid is more or less resolved into carbon dioxide and resorcinol.

This dihydroxybenzoic acid crystallises from water in long needles, containing $C_7H_6O_4 + 1\frac{1}{2}H_2O$. It melts at 194° , is very easily soluble in hot, but very sparingly in cold water. The hot saturated solution solidifies on cooling. The acid is also readily soluble in alcohol and ether, and gives a characteristic dark red colour with ferric chloride.

The following table exhibits the orientation of the substituted groups in the three dihydroxybenzoic acids whose structure has been made out, and the products which they yield by fusion with potash:—

	COOH.	OH.	OH.
Hydroxysalicylic acid	1	2	5 yields quinol.
Protocatechuic acid	1	3	4 „ catechol.
Dihydroxybenzoic acid. . . .	1	2	4 „ resorcinol.

The structure of the fourth dihydroxybenzoic acid, which Barth and Senhofer obtained from the corresponding disulphobenzene acid has not yet been established.

H. W.

Oxidation of Isocymenesulphonic Acid. By R. MEYER and H. BAUER (*Ber.*, **14**, 1135—1139).—The potassium isocymenesulphonate described by Jacobsen (this Journal, **36**, 624) when oxidised

by potassium permanganate, yields potassium hydroxypropylsulphobenzoate, $\text{COOK.C}_6\text{H}_3(\text{SO}_3\text{K}).\text{C}_3\text{H}_6.\text{OH} + 5\text{H}_2\text{O}$, identical with that obtained from cymenesulphonic acid by Meyer and Bauer (this vol., 45). This, together with the fact that isocymenesulphonic acid contains an isopropyl-group, shows that Meyer and Bauer were correct in attributing the formation of this acid to inter-molecular changes taking place in cymenesulphonic acid (*loc. cit.*) during its oxidation.

P. P. B.

Sulphoterephthalic Acid. By IRA REMSEN and W. BURNEY (*Amer. Chem. J.*, **2**, 405—413; further by Remsen and Kuhara, *ibid.*, 413—416).—This acid is produced by oxidation of sulphamineparatoluene or of cymenesulphonic acid with potassium permanganate (this Journal, 1880, Abstr., 257). The acid potassium salt, which is the immediate product of the reaction, yields by precipitation with

barium chloride the secondary barium salt, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{COH} \\ \text{CO}_2 \\ \text{SO}_3 \end{array} \right\} > \text{Ba} + \text{H}_2\text{O}$;

and this when heated with water and barium carbonate is converted into the normal or tertiary barium salt, $\left[\text{C}_6\text{H}_3 \left\{ \begin{array}{l} (\text{CO}_2)_2 \\ \text{SO}_3 \end{array} \right\} \right]_2 \text{Ba}_3 + \text{H}_2\text{O}$, which is quite insoluble in cold, and only slightly soluble in hot water. The primary barium salt, $\left[\text{C}_6\text{H}_3 \left\{ \begin{array}{l} (\text{CO}_2\text{H})_2 \\ \text{SO}_3 \end{array} \right\} \right]_2 \text{Ba} + 5\text{H}_2\text{O}$, is formed by treating the secondary salt with strong hydrochloric acid, which dissolves it readily at a gentle heat, the solution on cooling depositing the primary salt in well-formed crystals.

Normal or tertiary potassium sulphoterephthalate, $\text{C}_6\text{H}_3(\text{CO}_2\text{K})_2\text{SO}_3\text{K}$, obtained by neutralising the primary salt with potassium carbonate, is very soluble in water, and has not been obtained in crystalline form, but separates from very strong solutions in white warty masses. The secondary potassium salt has not been obtained pure. On neutralising one half of a solution of the primary salt with potassium carbonate, then adding the other half, and evaporating, a product was obtained, which proved to be a mixture of the primary and secondary salts; and when a solution of the primary salt was mixed with the exact quantity of potassium carbonate required to form the secondary salt and evaporated, the salt which separated was not uniform in composition, but appeared to be a mixture.

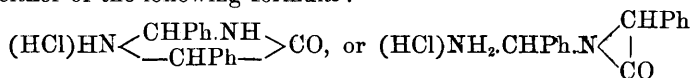
On treating the dry potassium salt of sulphoterephthalic acid with chlorine and ammonia in succession, a substance is obtained, which crystallises from water in long delicate needles, sparingly soluble in cold, more freely in hot water, and agreeing in composition with the

formula $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CONH}_2 \\ \text{SO}_2 \\ \text{CO} \end{array} \right\} > \text{NH}$, which is that of the amide of sulphinido-terephthalic acid (Remsen and Burney).

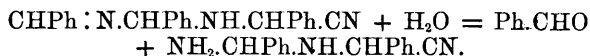
Sulphoterephthalic acid is also produced by oxidation of paraxylene-sulphonic acid with chromic acid mixture (Remsen and Kuhara).

H. W.

Action of Hydrocyanic Acid on Hydrobenzamide. By J. PLÖCHL (*Ber.*, **14**, 1139—1143).—By heating in a water-bath the ethereal solution of hydrobenzamid (1 mol.) with hydrocyanic acid (1 mol.), a di-imidomononitril is obtained; its hydrochloride separates out as a crystalline precipitate when hydrochloric acid gas is passed into its ethereal solution. The hydrochloride is very unstable, and when it is boiled with hydrochloric acid, the anhydro-acid is obtained, the constitution of which may be represented by either of the following formulæ:—

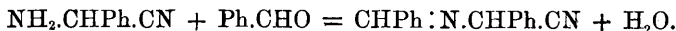


It is soluble in hot water or alcohol, and crystallises in slender needles, resembling asbestos. Aqueous ammonia precipitates the free acid from its solution. The acid is soluble in alcohol, and crystallises in needles (m. p. 120°); it loses water over sulphuric acid, and at 100° is resolved into the anhydride (m. p. 164°) and water. The formation of the anhydro-acid is explained (1) by the decomposition of di-imidomononitril into benzaldehyde and an amidonitril, thus:—



The amido-nitril is then converted into an acid by the decomposition of the "CN" group, and the acid so formed loses water, forming an anhydride of the above constitution.

Beside the nitril described above and the di-imidodinitril (this vol., 168), a third product of the action of hydrocyanic acid in hydrobenzamide has been obtained, viz., the *benzoylazotide* of Laurent and Gerhardt (*Annalen*, **28**, 265) and the *hydrocyanbenzide* of Reinecke and Beilstein (*ibid.*, 136—173). It owes its formation to secondary reactions, and is obtained when water slightly acidified or dilute hydrocyanic acid is added to di-imidodinitril (*loc. cit.*). The di-imidodinitril so treated is decomposed by boiling with strong hydrochloric acid into phenylamidoacetoneitril and benzaldehyde. These two compounds react to form *benzoylazotide*, $\text{C}_{15}\text{H}_{12}\text{N}_2$, thus:—



This constitution of benzoylazotide is shown (1) by its being resolved into phenylamidoacetic acid and benzaldehyde when boiled with strong hydrochloric acid, and (2) its formation from benzaldehyde and phenylamidacetoneitril [obtained by Tiemann's method from benzylidencyanhydrin (this Journal, **38**, 473)].

The author points out that Laurent and Gerhardt obtained this compound, owing to their benzaldehyde containing the cyanhydrin, which when treated with ammonia, would form phenylamidacetoneitril.

Benzoylazotide does not combine with hydrocyanic acid.

P. P. B.

Oxidation of Mesitylene-sulphonamide. By L. B. HALL and IRA REMSEN (*Amer. Chem. J.*, **2**, 130—143).—This amide boiled for several hours with chromic acid mixture is converted into *mesitylenic*

sulphinide $(\text{CH}_3)_2\text{C}_6\text{H}_2\text{SO}_2\text{NH}$, which separates from the resulting solution as a white crystallised body, and may be freed from a portion of the sulphonamide which remains unoxidised, by solution in sodium carbonate and precipitation with hydrochloric acid, and finally purified by crystallisation from water, from which it is deposited in short, thick, somewhat irregular lustrous prisms. It melts at 255° (corr. 262°), is almost insoluble in cold water, sparingly soluble in boiling water, easily in alcohol and ether. Like other sulphinides, when treated in aqueous solution with carbonates, it yields salts of the corresponding acid, sulphamine-mesitylenic acid. The *calcium salt* of this acid $[(\text{CH}_3)_2\text{C}_6\text{H}_2\text{SO}_2\text{NH}_2]_2\text{Ca} + 6\text{H}_2\text{O}$, crystallises in long, flat, transparent plates, easily soluble in water, soluble also in alcohol.

The *barium salt* is very soluble, and crystallises in groups of very delicate lustrous needles.

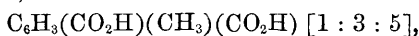
The *copper salt* $(\text{C}_9\text{H}_9\text{SO}_4)_2\text{Cu} + 4\text{H}_2\text{O}$, prepared from the barium salt by precipitation, forms radiate groups of small bright blue needles, which give off part of their water when dried in the air, the rest over sulphuric acid, and recover this last portion when again exposed to the air. At 200° , however, they give off all their water, and the bright green anhydrous salt does not recover it on subsequent exposure to the air. On adding silver nitrate to a dilute neutral solution of the ammonium salt, a heavy white precipitate is formed, containing, as a mean, 33.81 per cent. silver, which agrees in composition, not with silver sulphaminemesitylenate, but with the silver-derivative of mesitylenic sulphinide $(\text{CH}_3)_2\text{C}_6\text{H}_2\text{SO}_2\text{N} \cdot \text{Ag}$, which requires 33.96 per cent. silver.

Sulphamine-uvitic acid, $\text{C}_9\text{H}_9\text{NO}_6 = \text{CH}_3 \cdot \text{C}_6\text{H}_2 \begin{matrix} \text{SO}_2\text{NH}_2 \\ \text{COOH} \\ \text{COOH} \end{matrix}$, is obtained

in small quantity when the chromic acid oxidising mixture from which mesitylenic sulphinide has separated is left to itself for a while, or concentrated by evaporation on a water-bath; and more abundantly by gradually adding an excess of permanganate solution to mesitylenesulphonamide. It crystallises well from water in bunches of large transparent plates, is more readily soluble in water and in alcohol than the

sulphinide, and melts at 279° . Its *barium salt*, $\text{CH}_3 \cdot \text{C}_6\text{H}_2 \begin{matrix} \text{SO}_2\text{NH}_2 \\ (\text{COO})_2\text{Ba} \end{matrix} + 3\text{H}_2\text{O}$, is easily soluble in water, and has not been obtained in crystalline form. It gives off its water at 290° .

Sulphamine-uvitic acid heated in a sealed tube at 230° with strong hydrochloric acid, is converted into uvitic acid—



melting at 230° , and by fusion with potash into hydroxyuvitic acid (m. p. $294-295^\circ$).

Jacobsen (*Ber.*, **12**, 604; this Journal, 1879, Abstr., 643) by oxidising mesitylenesulphonamide with permanganate, obtained a mixture of

ortho- and para-sulphaminemesitylenic acid. Hall and Remsen likewise obtained these products, together with the bibasic sulphamine-uvitic acid, which is not mentioned by Jacobsen.

The paper concludes with speculations respecting the structure of the oxidation-products of mesitylenesulphonamide. H. W.

Naphthalene Derivatives. By F. GRAEFF (*Ber.*, **14**, 1061—1066). —Naphthonitril is prepared by heating a mixture of sodium naphthalene sulphonate and anhydrous potassium ferrocyanide in a flat copper retort. After washing the crude product with water, and distilling to remove ammonium cyanide and naphthalene, the nitril is obtained as a pale yellow oil (b. p. 280—290°).

By the action of strong nitric acid, it is converted into a mixture of mononitronaphthoic acid and nitronaphthonitril. This change is best effected by adding the naphthonitril to a cold mixture of 200 c.c. of nitric acid, sp. gr. 1.33, and 50 c.c. of fuming nitric acid, sp. gr. 1.48. To complete the reaction, it is necessary to warm the liquid.

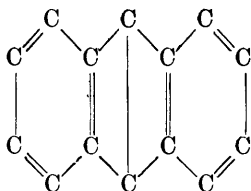
On pouring the solution into water, a yellow precipitate is thrown down, which is digested with potassium hydroxide, when the mononitronaphthoic acid dissolves, and the nitronaphthonitril remains. Nitronaphthoic acid is deposited from benzene in yellow needles (m. p. 200°).

By recrystallisation from absolute ether, the nitronaphthonitril can be separated into three portions which melt at 205°, 148°, and 100° respectively.

The chief fraction (m. p. 205°) is the least soluble in ether. It is sparingly soluble in light petroleum and carbon bisulphide, but dissolves freely in benzene, chloroform, alcohol, and glacial acetic acid. It is not acted on by sodium or potassium carbonate.

It is slowly saponified by alcoholic potash, rapidly by the action of strong hydrochloric acid at 120—130°, yielding *mononitro- α -naphthoic acid*, m. p. 238°, identical with the acid obtained by Ekstrand (*Ber.*, **12**, 1393; this Journal, 1880, Abstr., 261). W. C. W.

Synthesis of Anthracene and Phenanthrene from Orthobromobenzyl Bromide. By C. L. JACKSON and J. FLEMING WHITE (*Amer. Chem. J.*, **2**, 383—396). —Orthobromobenzyl bromide, $C_6H_4CH_2Br.Br.H_4$, warmed for some days with sodium, fresh portions of which are added from time to time, yields a mixture of anthracene and phenanthrene, together with dibenzyl, an oil consisting possibly of benzyl-toluene or ditolyl, and a viscous substance containing bromine. This synthesis of anthracene confirms the conclusion, rendered probable by other considerations, that in this hydrocarbon the two carbon-atoms which connect the two benzene-rings, are attached to each ring in the ortho-position, as represented by the formula—



The synthesis of phenanthrene in the same manner confirms the ortho-attachment of the two additional atoms of carbon, previously demonstrated by the experiments of Japp and Anschütz (this Journal, 1880, Trans., p. 88). H. W.

Hydroxyanthranol. By C. LIEBERMANN and S. E. SIMON (*Ber.*, **14**, 1234).—By the action of ammonia and zinc-dust on hydroxyanthraquinone, a pale yellow fluorescent solution is obtained, from which

hydroxyanthranol, $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \\ CH \diagdown \end{array} C_6H_3.OH$, is precipitated on the ad-

dition of an acid. Hydroxyanthranol crystallises in needles which dissolve freely in alcohol and ether. It melts at 202—206° with partial decomposition.

Treated with acetic anhydride and sodium acetate, it yields a crystalline diacetic derivative, $C_{14}H_{18}O_2.Ac_2$ (m. p. 155°). W. C. W.

De-oxyalizarin. By C. ROEMER (*Ber.*, **14**, 1259—1263).—To prepare de-oxyalizarin, 50 grams of zinc-dust are added to 50 grams of 11 per cent. commercial alizarin paste dissolved in 800 grams of 2·5 per cent. aqueous ammonia, and the mixture is boiled for 10 minutes. A greenish-yellow liquid is thus obtained, which is not converted into alizarin by exposure to the air. On pouring this solution into 500 grams of hydrochloric acid diluted with 1,500 grams of water, de-oxyalizarin is thrown down as a white precipitate. This is dissolved in cold dilute alcohol, and on the addition of water, needles or plates (m. p. 208°) are deposited. An alkaline solution of this compound is oxidised on exposure to the air, forming alizarin.

De-oxyalizarin, $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \\ CH \diagdown \end{array} C_6H_2(OH)_2$, is soluble in alcohol,

ether, acetone, glacial acetic acid, sulphuric acid and alkalis.

The alcoholic solution forms a yellow precipitate with an alcoholic solution of lead acetate.

The triacetic derivative, $C_{20}H_{16}O_6$, crystallises in needles (m. p. 188°), which dissolve in alcohol and ether with a blue fluorescence.

W. C. W.

Examination of "Stuppfett." By G. GOLDSCHMIEDT and M. v. SCHIDT (*Wien. Akad. Ber.*, **83** [2], 7—28).—When mercury ores are smelted (in Idria), there is formed in the condensation chambers, besides metallic mercury, a product called "stupp" which, after the removal of adherent mercury, is returned to the muffles to extract a further quantity of the metal; and in the second sublimation there are found, along with the mercury and the "stupp" powder, heavy crystalline lumps of a tough dirty substance called "stuppfett." It is impregnated with a thick oil, is greasy to the touch, and leaves a transparent stain on paper. It burns away, forming a great deal of soot, and leaving only a small residue. It contains no metallic mercury.

This was treated by the authors with alcohol and divided into three parts, one insoluble, one soluble but deposited in crystals, and one

which, on evaporating the alcoholic mother-liquors, was left as a thick brown fluid.

The black granular crystalline insoluble part was boiled out with benzene, in which it all dissolved, with the exception of a small inorganic residue—consisting of mercury, mercury sulphide, iron, manganese, alumina, lime, magnesia, gypsum, and clay—the solution was evaporated down, and the dark crystalline residue dissolved in a large quantity of alcohol. It crystallised out in leaflets, and from its melting point (248°), its vapour-density (7.54), and the blue colour its quinone gave with concentrated sulphuric acid, was recognised as *chrysene*. (The body from “Stupp,” although of the same percentage composition as *chrysene* is not identical with it.)

The different hydrocarbons were separated from the crystalline portion by repeated fractional crystallisation of their picrates from alcohol, those with higher melting points being least soluble in that medium. The least soluble (m. p. 222°) yielded *pyrene* (m. p. $149-150^{\circ}$); in this Journal (**34**, 432) Fittig and Heintz give m. p. $148-149^{\circ}$. The authors, however, consider theirs to be purer, as they have crystallised it from large quantities of alcohol and sublimed it. The next picrate (m. p. 110°) gave the characteristic long beautiful needles of *idryl*.* The hydrocarbon from the next picrate (m. p. 144°) melted at 100° , and had the properties of *phenanthrene*. The picrates melting below 144° were decomposed with ammonia, distilled, reconverted into picrates, and repeatedly recrystallised. In this way *anthracene* (m. p. 213°), identified by formation of alizarin blue from its quinone (m. p. 270°), and *diphenyl* (m. p. 70°) were obtained. They were separated from one another by distillation with steam, the diphenyl passing over and leaving anthracene-picrate behind.

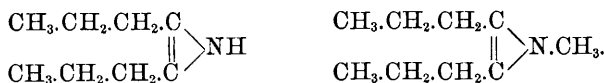
The fluid portion (7–8 litres) was repeatedly submitted to systematic fractional distillation, each fraction being cooled in snow, the crystals separated, and the mother-liquors refractioned, and in some cases fractionally precipitated with picric acid. By these means the authors isolated—*naphthalene* (m. p. 70° ; picrate, m. p. 149°); *diphenyl*; *diphenylene oxide* (m. p. $80-81^{\circ}$, b. p. $280-283^{\circ}$, uncorr., m. p. of picrate 94°), pleasant smelling large white leaflets; it was compared with and found like some prepared by Græbe's method, by distilling phenol with lead oxide; *acenaphthene*, long needles (m. p. 94° , m. p. of picrate 160°), agreeing in properties with Behr and Van Dorp's (*Annalen*, **172**, 263); *quinoline*, identical with Weidel's from cinchonic acid and Skraup's from aniline, &c.; the picrate melted at 203° , the platinochloride crystallised with 2 mols. H_2O ; *methyl-naphthalene*, (b. p. $230-231^{\circ}$)—Fittig and Remsen (*Annalen*, **155**, 114) found it to be $231-232^{\circ}$ —the picrate melts at 119° , Ciamician (*Ber.*, **11**, 272) gives $116-117^{\circ}$; *ethyl-naphthalene* (b. p. between $252-260^{\circ}$), Fittig and Remsen (*loc. cit.*, 119) give $251-252^{\circ}$, and Carnelutti (*Annalen*, **13**, 1671) $257-259.5^{\circ}$; they give the melting point of picrate 98° , the authors at 99° . There was another liquid body present, but all attempts to separate or examine it were unsuccessful. 32 kilos. of “stuppfeet” were employed. These substances were present in the following per-

* Identical with Fittig's fluoranthrene (*loc. cit.* and *Annalen*, **193**).

centages :—chrysene 0·1, pyrene 20·0, idryl 12·0, anthracene 0·1, phenanthrene 45·0, diphenyl 0·5, acenaphthene 0·003, naphthalene 3·0, methyl naphthalene 0·005, ethyl-naphthalene 0·003, diphenylene oxide 0·3, quinoline 0·003, inorganic constituents 0·5. D. A. L.

Synthesis of Methylconine, and Constitution of Conine.

By A. MICHAEL and C. GUNDELACH (*Am. Chem. J.*, 1880, **2**, 171).—H. Schiff in 1871—2, by leaving a mixture of normal butaldehyde and alcoholic ammonia to itself for six months, and heating the resulting bases to a high temperature, obtained, amongst other products, a tertiary base isomeric with conine, which he called *paraconine*. The authors obtain this base more readily by heating normal butylidene chloride, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHCl}_2$, with alcoholic ammonia for six hours at 180° . By using methylamine in this reaction instead of ammonia, a base is obtained which, from its physical properties and reactions, appears to be identical with natural methylconine. This is shown especially by the fact that when heated on a water-bath with ethyl iodide and alcohol, it yields a solid addition-product, apparently identical with the ammonio-iodide which Planta and Kekulé obtained in like manner from natural methylconine. From these and other reactions the authors assign the following formulæ to conine and methylconine :—



H. W.

Action of Selenium on Nicotine. By A. CAHOURS and A. ÉTARD (*Compt. rend.*, **92**, 1079—1084).—When 100 parts nicotine and 20 parts selenium are heated together for some time at 240° and then briskly boiled, the condensing tube becomes filled with white lamellar crystals, which may be sublimed. When the vapour is heated nearly to redness it is decomposed into ammonia and selenium. As soon as these crystals cease to form, the heating is discontinued, and the liquid is decanted from the undissolved selenium and distilled. Oily products pass over above 150° , and a tarry residue is left in the retort. These products are freed from selenium by adding a solution of soda and distilling in a current of steam, the receiver being changed as soon as the distillate becomes distinctly milky. The oily substances are separated from the water by means of ether, and again distilled. In this way *hydrocollidine*, $\text{C}_8\text{H}_{13}\text{N}$, is obtained as an amber limpid liquid (b. p. 205°), with a penetrating odour and burning taste. It is insoluble in water, but dissolves in alcohol, ether, and dilute acids. From acid solutions potassium hydroxide precipitates hydrocollidine. With iodine it gives a brownish-red precipitate, and with mercuric chloride a white precipitate soluble on heating. *Hydrocollidine aurochloride*, $\text{C}_8\text{H}_{13}\text{N}\cdot\text{HCl}\cdot\text{AuCl}_3$, is a yellow precipitate, which melts in warm water, dissolves at 100° , and is deposited in crystalline plates on cooling. The *platinochloride*, $(\text{C}_8\text{H}_{13}\text{N}\cdot\text{HCl})_2\text{PtCl}_4$, is an orange-yellow crystalline precipitate, soluble in hot water, from which it is deposited in brilliant plates. The other product of the action of selenium is

isodipyridine. It is probable that the selenium acts on the nicotine in the same way as sulphur, removing the hydrogen as hydrogen selenide, and forming isodipyridine thus: $C_{10}H_{14}N_2 + Se_2 = 2SeH_2 + C_{10}H_{10}N_2$. The hydrogen selenide then combines with unaltered nicotine, forming a hydroselenide which removes one atom of nitrogen in the form of the ammonia-compound described above. When nicotine hydroselenide is subjected to dry distillation, it yields the same products as those obtained by the action of selenium on nicotine. Nicotine when boiled alone does not give off ammonia.

The collidine obtained by passing vapour of nicotine through a red-hot tube (this vol., 672) boils at 170° , and shows a great tendency to form resinous polymerides. When oxidised by means of permanganate it yields nicotinic acid, and is therefore one of the propylpyridines corresponding with the isomeric position of nicotinic acid.

C. H. B.

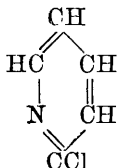
Action of Chloroform on Potassium-Pyrroline. By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, **14**, 1153—1163).—*Isochloropyridine*, C_5H_4ClN , is the base obtained by acting on potassium-pyrroline with chloroform; the action is violent, and anhydrous ether is used to moderate it. The base is a mobile, heavy, strongly refractive liquid, of penetrating odour, resembling that of pyridine. It is slightly soluble in water, and is volatile in a current of steam. It boils at 148° (bar. = 743.5 mm.); its vapour-density is found to be 57 (calc. 56.75). Unlike pyrroline, it is not attacked by nitric or hydrochloric acid, and boiling with strong hydrochloric acid under $1-1\frac{1}{2}$ atmos. pressure is required to remove unaltered pyrroline. This base has an alkaline reaction, and forms very deliquescent salts. *Isochloropyridine hydrochloride*, $C_5H_4ClN.HCl$, forms colourless thick deliquescent crystals, having a vitreous lustre. Its solutions, like the salts of bromo- and dibromo-pyridine (Hofmann, *Ber.*, **12**, 988), are decomposed on boiling. The *platinochloride*, $(C_5H_4ClN.HCl)_2.PtCl_4$, is obtained from concentrated solutions as a precipitate of slender slightly coloured needles. If the solution is dilute, long needles containing 1 mol. H_2O are obtained. The aqueous solution of the platinochloride is decomposed by boiling, just as the platinochloride of pyridine is (Anderson, *Annalen*, **96**, 200), and a compound, $(C_5H_4ClNCl)_2.PtCl_2$, is obtained.

The action of chloroform on potassium-pyrroline may be expressed as follows:—



Attempts to replace the chlorine in the above base by hydrogen have failed; an addition-product is obtained, however, by treating an alkaline solution with sodium-amalgam, or by treating the base with hydrochloric acid and zinc. The action of nascent hydrogen is attended with formation of ammonia. Weidel observed a similar phenomenon in the case of pyridine-carboxylic acid (*Ber.*, **10**, 201). The base thus produced is volatile in steam, and is separated from the ammonia by fractional precipitation of the mixed chlorides with platinum chloride. Its *platinochloride*, $(C_5H_{10}ClN.HCl)_2.PtCl_4$, separates from concentrated solution in golden-yellow leaflets, and from

dilute solution in thick orange-red crystals, containing 1 mol. H_2O , which they lose on exposure to the air. It would thus appear that the base takes up six atoms of hydrogen. Methylene chloride has no action on potassium-pyrroline. If Baeyer's formula for pyrroline (*Ber.*, 8, 517) be accepted, then the constitution of isochloropyridine will be—



whereas, if we accept Schiff's formula for pyrroline (*Ber.*, 10, 1193,

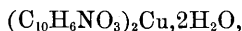
1560), it will have the formula $\begin{array}{c} \text{CCl} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{HC} \quad \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$, which the authors regard as

more probable. The fact that pyrroline combines with the group CCl , the authors regard as showing pyrroline to be a triad radicle, and hence it must contain one double linkage only.

A base very similar in its properties to isochlorpyridine has been obtained by the action of chloroform on the potassium compound of homopyrroline (methylpyrroline). It is a colourless liquid (b. p. $160-170^\circ$), slightly soluble in water, having a penetrating odour. It has a strongly alkaline reaction, and forms salts whose aqueous solutions are decomposed by boiling. Its *platinochloride*, $(\text{C}_6\text{H}_6\text{ClN}, \text{HCl})_2\text{PtCl}_3$, forms orange-red crystals.
P. P. B.

Kynuric Acid. By M. KRETSCHY (*Wien. Akad. Ber.*, 83 [2], 171—199).—A preliminary notice on this subject has already appeared in abstract in this Journal (38, 44). This acid is prepared from the filtered urine of dogs, which have been fed on parboiled meat; by acidulating the urine with hydrochloric acid, and allowing it to remain at rest for 24 hours, a yellow or brown precipitate is formed, which is dissolved in ammonia and the acid reprecipitated. It is purified by repeatedly crystallising the barium salt, dissolving up again, reprecipitating, &c., and finally by boiling the ammonia salt with animal charcoal, and precipitating with acetic acid. The pure acid, $\text{C}_{10}\text{H}_7\text{NO}_3 + \text{H}_2\text{O}$, crystallises apparently in rhombic prisms, giving up their water of crystallisation at $140-145^\circ$, and melting with slight frothing at $257-258^\circ$. It is almost insoluble in cold, and only sparingly soluble in hot water (1,000 parts of water at 99.6° dissolve 0.9 part), easily in alkalis or alkaline carbonates. It forms well characterised neutral salts. The *barium salt*, $(\text{C}_{10}\text{H}_6\text{NO}_3)_2\text{Ba}, 4\frac{1}{2}\text{H}_2\text{O}$, crystallises in scales or needles, sparingly soluble in cold water, easier in hot; it loses its water of crystallisation at $150-155^\circ$. The crude barium salt forms brilliant scales, which when many are aggregated together have a characteristic metallic lustre; whilst some pure salt prepared by heating the acid

with barium carbonate was obtained in thick needles, 1 cm. in length. The *calcium salt*, $(C_{10}H_6NO_3)_2Ca + 2H_2O$, forms snow-white needles, more soluble than the barium salt; the $2H_2O$ go off at $140-145^\circ$; on heating in a current of hydrogen, kynurine is formed, and the salt does not carbonise. The silver salt behaves in a similar manner, but the barium and copper salts carbonise. The *copper salt*,



is precipitated in yellowish-green microscopic needles, scarcely soluble in water (1.5 litre dissolving only 80 mgrams.); it gives up its 2 mols. H_2O at 145° . The *silver salt*, $C_{10}H_6NO_3Ag \cdot H_2O$, is a white precipitate, less soluble than the free acid; on heating it turns brown before losing all its water of crystallisation. The *ammonium salt*, $C_{10}H_6NO_3 \cdot NH_4$, is very soluble; the solution shows great tendency to decompose, and on evaporating down the ammonia is given off.

The *potassium salt*, $C_{10}H_6NO_3K + 2H_2O$, crystallises in deliquescent needles, is very soluble, and loses its water at $145-150^\circ$.

Kynurine, C_9H_7NO , prepared by heating kynuric acid for some time at $253-258^\circ$ in a current of hydrogen, and extracting with hot water, forms either colourless, brilliant, monosymmetric prisms* with no water of crystallisation, or (when it crystallises out suddenly) deliquescent needles with $3H_2O$, which it loses at $110-115^\circ$. It is sparingly soluble in cold water, ether, petroleum-ether, and benzene, very easily in warm water and alcohol (100 parts water at 15° dissolve 0.477 part). It fuses at 201° , and resolidifies at $159-160^\circ$; the needles fuse in their water of crystallisation at 52° . It decomposes when heated to 300° without distilling; under reduced pressure, however, it can be distilled with only slight decomposition.

Kynurine reacts slightly alkaline. It tastes bitter. Ferric chloride colours its solutions carmine, ferrous sulphate turns them yellow, and Millon's reagent gradually produces yellow-green coloration.

The *hydrochloride*, $(C_9H_7NO)_2 \cdot HCl + 2H_2O$, crystallises in large monosymmetric prisms* or glistening needles; they deliquesce and react acid; the *platinochloride*, $(C_9H_7NO, HCl)_2 \cdot PtCl_4 + 2H_2O$, is precipitated in sulphur-yellow microscopic needles, sparingly soluble in water, more easily in alcohol; it loses its 2 mols. H_2O at 110° ; but if it is exposed to the air it re-absorbs them.

The following experiments were made to prove the phenolic character of kynurine. With potassium it forms a crystalline substance, which has not yet been properly examined. With acetic chloride it forms a compound which is decomposed by water. With acetic anhydride it formed a similar body, which on decomposing yields kynuric acid (kynuric acid heated at 140° with acetic anhydride turns blood-red, then violet, ultramarine, and purple-red; the products cannot be separated without decomposition). A mixture of 2 parts phosphorus pentachloride and 6 parts phosphoric oxychloride, acts readily on kynurine (1 part), and yields a chlorine substitution-product, which is very easily decomposed; its *platinochloride*, $(C_9H_6NCl, HCl)_2 \cdot PtCl_4 + 2H_2O$ (losing its water at 100°) was analysed. By carefully distilling kynurine with 50 times its weight of zinc-dust, 62 per cent. of the

* Crystals marked thus have been measured by v. Lang.

theoretical quantity of *quinoline* were obtained. This quinoline boils between $234\text{--}235^\circ$ (uncorr.), or $240\cdot37\text{--}241\cdot33^\circ$ (corr. by Kopp's plan). $\text{Br}_2 = 750\cdot1$, and has all the properties of cinchonine quinoline. Treated with sodium-amalgam, kynurine yields a yellow substance, and a small quantity of a red dye-stuff. The yellow substance, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$ (m. p. 100°), is a powder, insoluble in sodium hydroxide, soluble in alcohol, has only very feeble basic properties, and contains no water of crystallisation.

Hydrochloric acid and tin convert the kynuric acid into kynurine; this into quinoline, and the latter into a liquid base; the analysis of its *hydrochloride*, $\text{C}_9\text{H}_{11}\text{N}\cdot\text{HCl}$, shows it to be tetrahydroquinoline; this salt crystallises in colourless long needles.

The author thinks it probable that the kynuric acid in the dog's urine is derived from the albumin; and that, hence, the complicated molecule of the latter contains amongst others also a nucleus of the quinoline series.

D. A. L.

Note.—The probability suggested by Weidel and Cobenzl (this vol., p. 744) is now verified: kynuric acid being the third hydroxy-quinolinecarboxylic acid, and kynurine the second quinophenol.

D. A. L.

Transformation of Morphine into Codeïne and Homologous Bases. By E. GRIMAUX (*Compt. rend.*, **92**, 1140—1143 and 1228).—When 1 mol. morphine is dissolved in alcohol containing 1 mol. sodium hydroxide, 2 mols. methyl iodide added, and the mixture gently heated, an energetic reaction takes place, the main product of which is codeïne methiodide, $\text{C}_{17}\text{H}_{18}\text{NO}_2\text{OCH}_3\cdot\text{MeI}$, identical with the compound formed by the direct union of codeïne with methyl iodide.

When only half the above quantity of methyl iodide is employed, free codeïne is obtained; but the yield is only small, since the greater part of the methyl iodide combines with the morphine, forming morphine methiodide. The codeïne thus artificially prepared is identical in chemical properties and crystalline form with the codeïne extracted from opium. Its molecular rotatory power for $[\alpha]_D = -130\cdot34^\circ$ approximately; that of natural codeïne being $-133\cdot18^\circ$.

If ethyl iodide is substituted for methyl iodide in the above reaction, a new base, $\text{C}_{19}\text{H}_{23}\text{NO}_3$, homologous with codeïne, is obtained. It crystallises with 1 mol. H_2O in hard brilliant plates, which are slightly less soluble in boiling water than codeïne, but dissolve readily in alcohol and ether. It melts at 83° , forming a limpid liquid which does not crystallise on cooling; at 100° it becomes brown, and is decomposed. The hydrochloride crystallises in mammillary groups of fine needles. The base is precipitated from solutions of its salts by potassium hydroxide and the alkaline carbonates, but not by ammonia.

Careful study of the properties of morphine leads to the conclusion that it is analogous to phenol. From this point of view codeïne is the methylic ether of morphine, and the new base is the ethylic ether. A whole series of such ethers may exist, and for these the author proposes the generic name *codeïnes*. Codeïne will then be *codomethylene*, and the new base will be *codethylene*.

Bochefontaine has found that codethylene acts as a poison, producing convulsions.
C. H. B.

Cinchotine and Hydrocinchonidine. By C. FORST and C. BÖHRINGER (*Ber.*, 14, 1266—1270).—Cinchonine and cinchotine are most easily separated by the fractional crystallisation of their sulphates. Cinchotine is not contained in commercial cinchonine, but is formed by the oxidation of cinchonine with potassium permanganate.

The following table shows the difference in solubility of five of the cinchonine and cinchotine salts.

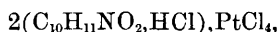
Parts of Water required to dissolve one part of the Crystalline Salt.

	Temp.	Cinchotine.	Cinchonine.
Sulphate	13°	30·5	65·5
Tartrate.....	16	56·8	33·0
Acid tartrate.....	16	78·0	101·0
Oxalate	10	86·0	104·0
Hydrochloride	10	47·2	24·0

The oxalate and hydriodide of cinchotine crystallise with H_2O . The acid tartrate which contains 4 mols. H_2O , and the anhydrous benzoate form needle-shaped crystals.

By treating chemically pure cinchonidine sulphate with potassium permanganate, cinchotenidine, and a new alkaloid, *hydrocinchonidine*, are produced. Hydrocinchonidine bears the same relation to cinchonidine that cinchotine does to cinchonidine. It crystallises in needles (m. p. 225°), and is distinguished from cinchotine by its greater solubility in alcohol, by its lævogyatory action on polarised light. The tartrate and thiocyanate are sparingly soluble.
W. C. W.

Tetrahydrocinchonic Acid. By H. WEIDEL (*Wien. Akad. Ber.*, 83 [2], 41—44).—If cinchonic acid (20 grams) mixed with zinc chloride (10 grams) is heated with hydrochloric acid (100 grams) and tin (28 grams) until the liquid, which turns orange-yellow, is decolorised, the excess of hydrochloric acid driven off on a water-bath, and the tin removed by sulphuretted hydrogen, then on evaporating down the solution to a thin syrupy consistency, the *hydrochloride of tetrahydrocinchonic acid*, $\text{C}_{10}\text{H}_{11}\text{NO}_2\cdot\text{HCl} + 1\frac{1}{2}\text{H}_2\text{O}$, crystallises out in large glistening, monoclinic plates,* which turn slightly red in the air, and are easily soluble in water and alcohol; ferric chloride colours the aqueous solution brown-green; on standing it first turns green, and then again becomes colourless. The *platinohydrochloride*,



crystallises in small dark yellow leaflets. The free acid was not obtained pure, its solution becomes discoloured on evaporation. Distilled with excess of lime it yielded, apparently, tetrahydroquinoline. With dehydrating agents carbonic anhydride and water are eliminated;

* Measured by Brezina.

and a base is formed containing C_{19} and resembling the cinchona alkaloids. D. A. L.

Strychnine Sulphate. By C. RAMMELSBURG (*Ber.*, **14**, 1231—1232).—Commercial strychnine sulphate, $C_{21}H_{22}N_2O_2 \cdot H_2SO_4 + 2H_2O$, crystallises in needles. The water is expelled at 150° . To prepare the neutral sulphate, $(C_{21}H_{22}N_2O_2)_2 \cdot H_2SO_4$, a solution of the acid sulphate is divided into two equal portions, one half is precipitated by ammonia, and the precipitate is added to the other part of the solution and the mixture boiled. On cooling the liquid deposits the neutral salt in transparent prisms, containing 5 mols. H_2O . The crystals are anhydrous at 200° . By the spontaneous evaporation of an aqueous solution of this salt transparent pyramids belonging to the quadratic system are obtained. These crystals contain 6 mols. H_2O .

W. C. W.

Lupinine. By G. BAUMERT (*Landw. Versuchs.-Stat.*, **27**, 15—64).—This paper contains a very extensive series of observations and experiments on the alkaloids of the lupine, for many details of which reference must be made to the original paper. It commences with a review of previous investigations by other chemists, Cassola, Eichorn, Beyer, Siewert, Schultz, and chiefly Liebscher. Their conclusions differ in consequence of the substances examined containing a mixture of the alkaloids, two of which are capable of crystallisation; out of the fluid portion two substances have been isolated by Siewert and Schulz, with the composition $C_8H_{17}NO$ and $C_{17}H_{15}NO$, but the crystallisable body obtained by Liebscher, to which the author gives the name of *Lupinine*, has not been hitherto examined, and four formulæ have been proposed for the second alkaloid, that of lowest boiling point. The author records the result of his own examination of Liebscher's lupinine, a quantity of which of the purest nature he left behind on his departure for Japan. The preparation of the pure alkaloid is tedious. The crushed seeds are digested in alcohol with some hydrochloric acid to complete exhaustion; the extract evaporated to a syrupy consistence; the acid is neutralised with sodium hydroxide; solid potassium hydroxide is added; the mixture treated with an equal volume of light petroleum, shaking at intervals for the space of a day; and the extraction with petroleum process is repeated 20 to 25 times. The light petroleum is agitated with hydrochloric acid, which dissolves the alkaloid as hydrochloride, and leaves the colouring matter and fat; the clear aqueous solution is again treated with potassium hydroxide and shaken up with ether; on evaporation, this leaves the nearly pure substance as a brown syrupy liquid, which quickly crystallises. It may be purified by recrystallisation from pure ether. 4 centners of the seeds yielded about 750 grams of the mixed alkaloids.

Lupinine is a strong base, liberating ammonia from ammonium chloride solution, combining readily with acids, and giving dense white fumes on the approach of a glass rod moistened with dilute hydrochloric acid. It is very easily crystallisable, and the shape of the crystals varies according to the concentration of the solution. From its solution tannic acid throws down a flocculent precipitate, phosphomolybdic and phosphotungstic acids a yellow, iodine from aqueous

solution a dirty brownish-red. Lupinine in combination has an intensely bitter taste; the free base is very caustic, and has an agreeable smell resembling apples; its physiological effect is to paralyse certain nerve-centres; it has a lævorotatory action on polarised light. It is easily soluble in cold water and in alcohol, less so in warm water; freely soluble in benzene, chloroform, and similar fluids; carbon disulphide not only dissolves the crystals but acts chemically on them. The melting point is from 67.5° to 68.5° , and the boiling point ranges, according to the purity of the substance, from 255° to 261° . Lupinine distils unaltered in a current of steam or of hydrogen.

The elementary analysis of *lupinine* is somewhat difficult, but the author succeeded in establishing a formula different from those of previous experimentalists, viz., $C_{21}H_{40}N_2O_2$, which is confirmed by examinations made of its salts; of these the platinochloride, aurochloride, the sulphate (neutral and acid), nitrate, and picrate were analysed.

The behaviour of lupinine with ethyl iodide was first investigated by Siewert, who inferred from his results that a tertiary base was produced, and called it ethyl-dimethylconidriammoniumiodide, with the formula $C_{10}H_{21}NO, C_2H_5I$. The author's analyses of the product led him to conclusions slightly different, and pointed to a body of the composition $C_{26}H_{50}N_2O_2I_2$, which agrees with his previous examination of lupinine itself. An opinion was at one time current that lupinine was a derivative of the hemlock alkaloids, but this opinion does not rest on any chemical evidence.

J. F.

Peptones and Alkaloids. By C. TANRET (*Compt. rend.*, **92**, 1163—1165).—Solutions of peptone, obtained either by means of pancreatin or pepsin, give, with the ordinary reagents for the alkaloids, precipitates similar to those given by the alkaloids, but these precipitates are soluble in an excess of peptone, whereas the precipitates given by the alkaloids are not soluble in excess of the latter. Coagulated white of egg dissolved in sodium hydroxide solution, after neutralisation of the free base and filtration, yields a solution which gives all the reactions of the peptones. This modified albumin, like peptone, is not precipitated by lime; peptone, moreover, is somewhat soluble in alcohol. Other albuminoids will probably behave in the same way. It follows, therefore, that a precipitate by potassium mercury iodide, in presence of free acid, by Bouchardat's reagent, bromine, water and tannin, in a solution previously treated with lime or alcohol to remove albuminoids, cannot be regarded as positive proof of the presence of an alkaloid.

When peptone is treated with potassium carbonate, or better, potassium hydroxide, and agitated with ether, the latter dissolves a small quantity of a substance having all the characters of an alkaloid. If the peptone is allowed to putrefy without becoming alkaline, a solid non-volatile alkaloid is formed. The hydrochlorides of both these alkaloids may be obtained crystallised. From salts of these alkaloids alkaline bicarbonates set free the bases, but the action of the bicarbonates on peptone does not give rise to alkaloids. It follows, therefore, that the latter do not exist ready formed in the peptone, but are the products of the action of the alkalis.

The alkaloïds derived from peptone give Brouardel and Boutmy's reaction, but, like the ptomaines, not instantaneously. Eserine, liquid hyoscyamine, and amorphous aconitine and ergotinine, give the reaction instantaneously: with digitaline and crystalline aconitine and ergotinine it is apparent only after a few seconds. This reaction cannot therefore be employed to distinguish between animal and vegetable alkaloïds.

C. H. B.

Crystalline Albuminoïds from Different Oil Seeds. By H. RITTHAUSEN (*J. pr. Chem.* [2], 23, 481—486).—The author has already communicated results from the press-residues of the earth-nut, *Arachis hypogæa*, *Sesamum indicum*, coconut, sunflower seeds, (*Helianthus annuus*), &c. (this Journal, Abstr., 1880, 676).

By extracting hemp-cake with a 10 per cent. solution of sodium chloride at the ordinary temperature, and adding water to the extract, a precipitate is formed, then by treating this with a warm 20 per cent. solution of sodium chloride part is dissolved, and the solution deposits, on cooling, an albuminoïd crystallising in octohedrons and other forms of the regular system, soluble in water, and probably identical with Grübner's substance from pumpkin seeds which, however, is not mentioned as soluble in water. 3,000 grams of hemp-cake yield 75 grams of crystals. From the press-residues of the castor-oil seed, a small quantity of crystals, apparently identical with the above, was extracted. From sesame seed residues the extraction with salt solution is made at 40°, the albuminoïds not being very soluble at ordinary temperature; a very small quantity of crystalline albuminoïd was obtained, mixed with non-crystalline substance. On examining the crystals microscopically they were found to be octohedrons, but of different dimensions from the above, and the author infers therefore that they are not identical. Salt solution extracts from earth-nuts a considerable quantity of an albuminoïd, precipitated by water in globules, which behaves quite differently from the crystalline hemp-albuminoïd. Sunflower seeds and their press-residues, cotton-seed cakes, hazelnuts, and candlenuts and their press-residues, also give globular and not crystalline deposits.

D. A. L.

Physiological Chemistry.

Influence of Light on Chemical Action in Animals. By J. MOLESCHOTT and others (*Bied. Centr.*, **10**, 94—96).—From experiments conducted on blind and on uninjured animals, the authors conclude that the evolution of carbonic anhydride is aided by light, whether acting on the eyes or on the skin. The following numbers were obtained for the evolution of carbonic anhydride in experiments on various animals:—

	Uninjured.		Eyeless.	
	In dark.	In light.	In dark.	In light.
Batrachians	100	120	100	111
Birds	100	134	100	127
Mammalia	100	140	100	112

The intensity of the light also increases the production. The same action takes place in the fresh muscle of frogs and mammalia. Coloured light produces different effects on cold and warm-blooded animals. Violet light acts in the same way as white light; red light had no effect on frogs. Heat, in the case of warm-blooded animals, lessens the production of carbonic anhydride, but increases it in the cold-blooded.

Speck has made experiments on the same subject on himself: there was, however, the greatest difficulty in ensuring absolute rest from muscular movement; but the general results confirm what is stated above with reference to mammalia.

J. K. C.

Influence of Certain Salts and Alkaloids on Digestion. By L. WOLBERG (*Pflüger's Archiv.*, **22**, 291—310).—The experiments consisted in a series of observations on artificial peptic digestions (glycerol extract of gastric mucous membrane, with hydrochloric acid and fibrin), to which the various salts were added, allowed to digest for 24—48 hours at 40—45° C., then filtered, and the residue dried and weighed; the results were compared with those of similar artificial digestion, to which no salts were added; the differences found were in all cases small. Chlorides, sulphates, and nitrates of the alkalis, and borax, and especially the latter, seem to retard digestion.

W. N.

Fattening of Sheep. (*Bied. Centr.*, **10**, 105—106).—To ascertain the best way of fattening sheep when the chief fodder consisted of turnip-cabbage, a flock consisting of 102 wethers and 48 sheep was divided into six lots as equally as possible, and each lot fed with as much turnip-cabbage as they could eat, and the following quantities of bye-fodder daily: Lot 1, 15 kilos. hay; lot 2, 15 kilos. lupine hay; lot 3, 6 kilos. ground lupines; lot 4, 5·5 kilos. rape-meal; lot 5, 2·5 kilos. flesh-meal; lot 6 received no additional fodder until after 44 days from the commencement of the experiment, when the sheep were fed with 6 kilos. ground rye daily. At the end of two months it was found that flesh-meal had given the best results, whilst in decreasing order follow lupine hay, meadow hay, rape-meal, ground lupines, and ground rye.

J. K. C.

Chemistry of Vegetable Physiology and Agriculture.

Non-existence of "*Microzyma cretæ*." By CHAMBERLAND and ROUX (*Compt. rend.*, **92**, 1165—1166).—Fragments taken by means of a sterilised auger from the freshly fractured surface of blocks of chalk from a deep gallery in the quarries at Meudon, were introduced into tubes containing a solution of sugar mixed with yeast, which had previously been heated at 35° for some time. In tubes containing a similar solution, pieces of ordinary chalk were placed. Some of the tubes were then heated to 115° and hermetically sealed or plugged with sterilised cotton-wool. After 24 hours all the flasks which contained ordinary chalk, and had not been heated, gave off gas and contained microscopic organisms, amongst which the lactic ferment could be distinguished. A portion of the sugar had been converted into lactic acid, the presence of which in the solution could be recognised. All the tubes containing chalk from Meudon, and all the tubes which had been heated to 115°, remained unaltered for a considerable time. It is evident that the chalk from Meudon behaves like chalk sterilised by heat, and does not contain germs of any microscopic organisms or ferments. From this it would appear that Béchamp's *Microzyma cretæ* does not exist. C. H. B.

Sterilisation of Animal and Vegetable Liquids. By P. MIQUEL and L. BENOIST (*Bull. Soc. Chim.* [2], **35**, 552—557).—Pasteur has proposed to render sterile liquids infested with bacteria by filtration through plaster of Paris; the authors have devised a simple method for working out this process. The neck of a flask is drawn out, and the part above the contraction is sealed by a plug of plaster of Paris and asbestos, and immediately below the contraction a fine capillary tube is drawn out at the side. The apparatus is then dried for a week or two at 40°, and finally heated to 170°, in order completely to destroy the germs on the sides of the flask and on the plug. When the flask is cooling, the capillary point is introduced under perfectly sterilised water, and on breaking it off, 40—50 c.c. of water pass up into the flask. The liquid is then boiled to expel the air completely from the flask, and the point is resealed, while at the same time the plug is introduced into the infested liquid. On cooling, the liquid passes into and fills the flask. The authors draw attention to various precautions which are necessary to ensure success. V. H. V.

Microscopic Researches on Yeast. By O. DURST (*Bied. Centr.*, **10**, 129—130).—The author has made hourly observations of the changes undergone in yeast mash during acid fermentation. The first traces of lactic ferment were observed in the mash at 42—44° R.; after 10 hours' acidification at 34° R. this ferment was strongly developed, the under beer ferment consisting of round full cells. When the fermentation was nearly over, butyric bacteria were observed in the liquor. When the cells were transferred into flasks, and the latter hermetically sealed, single cells were developed in great numbers. J. K. C.

Fermentation in Presence of Organic Salts. By A. MAYER and others (*Bied. Centr.*, **10**, 127—129).—Mayer observed that in 30 per cent. sugar solutions moist yeast cells lose their activity, and do not regain it when the solution is diluted; a small quantity of Rochelle salt, however, at once sets up an active fermentation. Other experimenters have sought to confirm the result that Rochelle salt promotes fermentation, but have failed to do so. J. K. C.

Influence of Succinic Acid on the Fermentation of Cane-sugars. By U. GAYON (*Bull. Soc. Chim.* [2], **35**, 501—503).—Yeast transforms cane-sugar into invert sugar, which then undergoes fermentation; but there are present two agents, Berthelot's fermenting principle and succinic acid, the presence of which Pasteur has indicated in such liquids. The author wishes to establish whether, in the absence of the former, the latter is sufficient to determine the fermentation. It was found that when a mixture of succinic acid, pure cane-sugar, and yeast was sealed up in Pasteur's flasks, 1st, that there is no inversion of sugar in presence or absence of fungoid growth; 2nd, that the quantity of sugar and succinic acid diminishes in the flasks in which the fungus has developed, thus showing that these bodies contribute to its growth. V. H. V.

Dissociation of Nitric Acid by Vegetation in the Dark. By BOUSSINGAULT (*Ann. Chim. Phys.* [5], **22**, 433—450).—It is well known that when the growth of plants takes place in the dark, the etiolated plant weighs less than the grain from which it has issued; and the tissue is impregnated with a liquid, showing an appreciable acid reaction. The cotyledons are provided with the necessary principles for embryonic existence, but are unable in the dark to fix the carbon from the atmospheric carbonic acid. It seemed desirable to ascertain whether under the same circumstances vegetable growth is equally unable to decompose other fertilising substances, usually found in the soil, such as the nitrates. To decide this point the author has executed a series of researches, which consisted in planting in a previously calcined soil of various nature, the seed of different plants, and watering the soil from time to time with a solution of potassium nitrate of known strength. The amount of ammonia in the plant was determined before and after the experiment, and the nitric acid

Experiment.	Nitrate disappeared for 1 of salt introduced.	Nature of soil.	Plants.	Time of vegetation in days.
I.	0.453	Pumice stone.	Beans.	24
IV.	0.650	Pumice stone.	Maize.	26
V.	0.460	Quartz sand.	Beans.	20
VI.	0.500	Quartz sand.	Maize.	22
VII.	0.795	Pumice stone.	Beans.	16
VIII.	0.800	River sand.	Maize.	16
IX.	0.300	River sand.	Wheat.	10
X.	0.785	River sand.	Maize.	10
I. (bis)	0.404	River sand.	Maize.	18

remaining in the soil or absorbed by the plants was compared with that originally introduced.

The table (p. 836) gives the results of the various experiments.

This table shows that, taking the mean, rather more than half the nitrate (0.57) originally introduced has disappeared during vegetation. The nature of the soil does not seem to exert any appreciable influence. The author does not offer any explanation of this decomposition of the nitric acid of potassium nitrate, but considers it at least probable that this change takes place at the contact of the roots with the soil, for in the experiment the amount of nitrate recovered in the plants was far greater than that recovered from the soil. The presence of fungus growth was throughout the experiments carefully avoided, and the roots presented both before and afterwards the same appearance. It was further observed that an etiolated plant, even after it had lost its vitality by being exposed to a current of steam, possessed this power of decomposing the nitrate.

V. H. V.

Action of Vapours on Seeds. By F. SESTINI (*Bied. Centr.*, 10, 135).—Kraus found that by subjecting sprouting seeds in the absence of light to the action of methyl alcohol, an artificial production of chlorophyll ensued. Sestini on repeating the experiment was unable to confirm this result.

J. K. C.

Torpid Condition of Seeds. By P. v. TIEGHEM and G. BONNIER (*Bied. Centr.*, 10, 135—137).—Of the many seeds examined, only those of the maple were found to be destroyed during a severe winter. When tubers of various plants were placed in closed vessels, after the oxygen had been absorbed, an evolution of carbonic anhydride was observed, and the presence of alcohol in the tissues was ascertained.

J. K. C.

Ash of Various Parts of a Plant. By A. VOGEL (*Bied. Centr.*, 10, 138).—The quantity of ash soluble in water is greatest in all the soft parts of a plant towards the end of the vegetating period. The least quantity is found in the wood, and the greatest in the leaves; the phosphoric acid varies very little in the leaf and stem, except in the case of the elder.

J. K. C.

Crushed Oats as Fodder. By E. BREYMANN (*Bied. Centr.*, 10, 133).—Experiments with 45 horses carried on for four years have led to the result that by using crushed oats, 3 lbs. a day less fodder are required than when whole oats are given.

J. K. C.

Stripping Maize. By F. v. OPPENAU (*Bied. Centr.*, 10, 109—110).—In many places before the maize ripens it is stripped to a great extent of its leaves, which make an excellent green fodder. Experiments, however, go to show that plants which have been thus stripped do not yield the normal quantity of corn.

J. K. C.

Colour of Clover Seed. By G. HABERLANDT (*Bied., Centr.*, 10, 135).—In order of value come first the bright yellow and violet seeds, next the grey and brownish, and worst of all the brown seeds.

J. K. C.

Purification and Digestibility of Lupines. By O. KELLNER (*Bied. Centr.*, 10, 97—105).—Lupine seeds can be deprived of the whole of their bitter constituents by consecutive soaking, steaming, and washing with cold water. The time necessary for each of these operations was found to be as follows: soaking for 24 hours, steaming for one hour, and two days' washing, with frequent stirring and renewal of the washwater. Ripe seeds lose under these circumstances 15—20 per cent. of their dry substance, this loss chiefly consisting of non-nitrogenous extractive matter; unripe and half-ripe seeds sustain much greater diminution, including considerable loss of valuable nutriment. In the case of ripe seeds, the detriment occasioned by the removal of a small percentage of nutritive substance is amply compensated by the improved quality of the remainder, as seeds so treated are not only devoured with great appetite, and without injury, but are also more digestible, and exercise a favourable influence on the assimilation of the raw fibre of the bye-fodder. The above method has received increased importance from the researches of Kühn, who has shown that those substances which cause lupine sickness are destroyed by steaming. J. K. C.

Analysis of Rice Soils from Burmah. By R. ROMANIS (*Chem. News*, 43, 237).—It was found that the amount of phosphoric acid in the soil in any one district corresponded pretty well with the settlement officer's valuation, but on comparing two districts it was found that the district which was poorer in phosphoric acid gave crops equal to the richer one. On inquiry it was found that in the former the rice is grown in nurseries and then planted out by hand, whereas in the latter, where the holdings are much larger, the grain is sown broadcast. The conclusions drawn from this investigation are that, climate and situation being equal, the value of soil depends on the phosphoric acid in it, and that the planting out system is far superior to the broadcast system of cultivation.

The following are the results of two analyses of soils from Syriam, near Rangoon. No. II is virgin soil:—

Soluble in Hydrochloric Acid.

	Organic matter.	Fe ₂ O ₃ and Al ₂ O ₃ .	MgO.	CaO.	K ₂ O.	Na ₂ O.	P ₂ O ₅	SO ₃ .	SiO ₂ .
I.	4.590	8.939	0.469	traces	0.138	0.136	0.100	0.025	—
II.	8.508	7.179	0.677	0.131	0.187	0.337	0.108	0.117	0.005

Soluble in Sulphuric Acid.

	Al ₂ O ₃ .	MgO.	CaO.	K ₂ O.	Na ₂ O.
I.	17.460	0.459	0.286	0.616	0.317
II.	15.684	0.446	traces	1.250	0.285

Residue.

	SiO ₂ soluble.	SiO ₂ insoluble.	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.
I.	11.675	—	49.477	3.062	0.700	0.212	0.276
II.	—	69.546	—	4.178	0.134	traces	1.180

These are alluvial soils, from the delta of the Irrawaddy.

D. B.

The Humus Extracted from Soil by Alkalis. By O. PITSCH (*Bied. Centr.*, 10, 75—82).—According to Grandeau, that part of the humus which exists in the soil in combination with bases is the source of mineral matter to growing plants, and the amount present may therefore be considered as a measure of the fertility of the soil. In order to estimate the quantity, soil is treated with dilute hydrochloric acid and washed, and the residue extracted with ammonia; the resulting solution is then evaporated to dryness, forming a black substance, which contains phosphoric acid, and is considered by Grandeau to correspond with the fruitfulness of the soil. This result has been found to be practically true in sandy, moor, and light loamy soils, and the object of this investigation is to ascertain its bearing in connection with heavy clay soils. In the 15 samples analysed, the first 12 gave results generally in accordance with Grandeau's theory, but the last three were at variance as regards the amount of phosphoric acid contained in the black substance, part of which had probably been removed by the hydrochloric acid. It was, however, not clear that the phosphates contained in the black substance were not first brought into solution during the process of examination, instead of originally existing in the soil in combination with humus substance; and it was found on further examination that a solution of humus in ammonia has the power of dissolving phosphates, especially those of iron and alumina. No evidence is therefore afforded in support of Grandeau's theory that the phosphoric acid extracted by ammonia existed originally in combination with humus substance.

J. K. C.

Employment of Potassium Salts as Manure. By M. MÄCKER (*Bied. Centr.*, 10, 87—94).—Recognising the fact that the use of potassium salts as manure has as yet obtained no extended application, the author has undertaken to inquire, by a comparison of data already obtained, whether the often noticed failure of this manure is due to a misunderstanding of results, and what special influence potassium salts have on the various field growths. In reference to the former question the author remarks that artificial manures, when applied alone, often fail to give their due result, and should be mixed with other kinds to ensure success; in cases where the soil is already rich in potassium salts, a direct improvement is of course not to be expected. As all the potassium in the soil is converted into silicate, it is of no importance whether the original salt be chloride or sulphate; in some cases, however, chlorides give the best results. The presence of magnesium chloride in dilute solution is no more injurious than that of potassium or sodium chloride. The indirect action of potassium salts is often very great; they act as solvents to the absorbed plant-food in the soil, keep the soil dry, and often induce early ripening of the fruit. Of the action of potassium salts on special plants, the following may be said:—

Oats.—The seven experiments were all successful; the oats ripened 8—10 days sooner, a better yield was obtained, and the corn weighed heavier. In this case raw chlorinated salts gave the best result.

Barley.—In two out of three instances a greatly increased yield was obtained; the corn was inclined to lie, because the ears were more highly developed than the stalk; in other ways the same results were obtained as with oats.

Peas.—Only one experiment was to hand, which gave very favourable results; in this case the ripening was delayed, but fewer of the plants perished, and the growth of weeds was diminished.

Maize.—The one experiment to hand was very successful; here again the presence of chlorides proved a distinct advantage.

Linseed.—All three experiments gave most favourable results. Chlorides were found to be preferable to other salts, and improved the quality of the fibre, as did also chloride of sodium; this action is probably due to the presence of chlorine.

Lupines.—In all cases good results were obtained; any kind of potassium salt will do, and, in opposition to what was observed in the case of all other plants, potassium salts produce the best effect when given alone; on marly soils it must not be applied later than December.

Mowing Grasses.—In combination with nitrogen and phosphate manures excellent results were obtained; an improvement of the quality was noticed, and a considerable after-effect in the second year.

Clover.—Here again, in addition to increase of yield, was noticed a diminution of weeds.

Turnips.—The results obtained were generally satisfactory, but unfavourable when the manure was applied late; potassium chloride was found to answer best, although sodium chloride answered nearly as well.

Potatoes.—In 24 out of 27 experiments a considerable increase of yield was observed, but in many cases there was a lowering of the starch percentage; to avoid this, the potassium salts, especially if containing much chloride, must be applied early, and must be tolerably free from impurities.

Beetroot.—In only half the experiments was the yield increased, and in very many the percentage amount of sugar was diminished. The amount of sugar was increased only where the yield in general was bad, either from poorness of the soil or oversowing; no particular effect was observed on the root disease.

Rye.—On light marly soils, in conjunction with phosphates and nitrogen manures, the results were always favourable.

On marshy soils, if well drained, the action of potassium salts is invariably successful in a very great degree; in lighter sandy soils, if given along with other manures, the results are equally satisfactory; in better soils potassium salts do not appear so necessary, but having regard to what has been said of their influence on various plants, they may still be used to great advantage. Of course to obtain good results, all disturbing influences, such as the presence of free acids or soluble iron salts in the soil, bad drainage, &c., must be removed.

J. K. C.

Manuring with Potassium Salts. By A. MAYER (*Landw. Versuchs.-Stat.*, 26, 321—351).—After considering at some length the means ordinarily employed in manuring experiments for the purpose

of obtaining trustworthy and practical results, the author goes on to show that where the experiments are carried on in small patches of ground separated by partitions of various kinds, those plants nearest to the dividing walls are necessarily placed under different conditions of growth to those which are further away, and consequently do not develop under the normal conditions of the experiment; some of the plants may also, owing to some accident, either die or have their growth considerably impeded, whilst the neighbouring ones will in consequence have an abnormally large space for their development. Other causes determined by external circumstances may also arise which may affect the growth of plants, and place some of them in abnormal conditions. On these grounds, therefore, it is best to select those plants which appear to be of average growth, and are nearer the centre of the plot, in order to obtain a trustworthy result. The value of this plan will of course depend on the correct judgment of the experimenter.

Following the principles already laid down, the author carried out several experiments with clover, millet, tobacco plants, potatoes and beet: the potash was applied in various forms, such as sulphate, chloride, silicate, and hydrate, with or without lime: in addition some other manure, superphosphate or Chili saltpetre, was used. The results varied considerably in the different plants under investigation: millet and tobacco, which were grown in almost pure sand, thrived best when a basic body, such as soda or lime, mixed with chloride of potassium, was applied; potassium sulphate did not give equally good results. This latter substance, however, answered best in the case of clover, whilst the former mixture proved decidedly injurious to the development of beetroot and potatoes, potassium chloride by itself producing a much better effect. As an example of the manner in which the details were carried out, the following experiment with beetroot may serve. A plot of ground 50 square meters in area was selected, and the soil dug out to the depth of half a meter, mixed with one-twelfth of its volume of sand and relaid. The plot was divided into 10 of 4 square meters, and one of 10 square meters: each 4 square meters was manured with 125 grams Chili saltpetre, and equivalent quantities

No. of plot.	Sort of manure.	Yield per hectare.	Sugar per hectare.	Non- sugar per cent.
		Kilos.	Kilos.	
1	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{KCl}$	62,667	6,166	3.0
2	$\text{NaNO}_3 + \text{CaHPO}_4 + \text{KCl}$	57,042	5,841	3.2
3	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{Ca}(\text{HO})_2$	67,365	6,824	3.3
4	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{KHO}$	63,288	5,588	2.9
5	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{potash turf}$	50,859	5,300	2.6
6	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{soluble potash glass}$	53,649	5,226	3.0
7	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2 + \text{KCl} + \text{Ca}(\text{HO})_2$	50,328	5,551	2.4
8	$\text{NaNO}_3 + \text{CaHPO}_4 + \text{KCl} + \text{Ca}(\text{HO})_2$	45,891	5,007	2.7
9	$\text{NaNO}_3 + \text{CaHPO}_4 + \text{potash turf}$	52,506	5,408	3.0
10	$\text{NaNO}_3 + \text{CaHPO}_4 + \text{Ca}(\text{HO})_2$	45,738	4,652	2.3
11	$\text{NaNO}_3 + \text{CaH}_4(\text{PO}_4)_2$	56,691	5,801	3.0

of superphosphate and potash salts as given in the table (p. 841), and contained 36 roots, of which the central eleven were chosen as yielding the most normal results. The plants were set on April the 8th, thinned on June the 11th, and the crop was gathered in on the 16th October. The plots were thoroughly weeded during the whole time: the kinds of manure and the yields are given in the table (p. 841).

J. K. C.

Potassium Salts as Manure for Grass. (*Bied. Centr.*, 10, 132.)—The agricultural station at Worms has collected the results of experiments by several pupils in various neighbourhoods. These experiments were conducted on different kinds of soil, at various situations and heights above sea level, on irrigated land or dry, and with both potassium sulphate and chloride.

Potassium sulphate, used both in late autumn and early spring, to the amount of 8 centners per hectare, gave an increase of 47 per cent. above the unmanured plots. Potassium chloride applied late in the autumn at the rate of 9 centners per hectare, raised the yield on the average 31 per cent., but when given in the early spring it showed no appreciable effect.

J. K. C.

Stable-dung as Manure for Beet. By M. MÄRCKER (*Bied. Centr.*, 10, 138).—When applied to the fields in autumn this manure yields very good results, both as regards the quality and quantity of the crop.

J. K. C.

Irrigation with Sewage. By A. MÜLLER (*Bied. Centr.*, 10, 83—86).—The object of this investigation was to ascertain the amount of water left in a sewage irrigation field after a lengthened period of dryness. The soil consisted chiefly of sand: free moisture was estimated by exposure of the soil to the air: hygroscopic water by heating the samples to 105°; the loss on ignition consisted chiefly of organic matter.

In eighteen samples, the free moisture varied from 0.4 to 8.8; the hygroscopic from 0.13 to 0.58, and the loss on ignition from 0.1 to 2.5 per cent., the last two varying pretty constantly with one another. The amount of plant-food in the soil was found to vary exactly with the quantity of adherent water, thus showing that the sand itself underwent little alteration from the sewage.

J. K. C.

Phylloxera Vastatrix and Means of Destroying it. By ROUSSET and others (*Bied. Centr.*, 10, 110—115).—Some cases are reported where infected vines after being left two or three years untouched, have finally recovered. Very often it is found that the labourers carry the insect from one field to another, and so spread the disease. In Hungary an experiment station for the purpose of investigating the disease and discovering the best means of prevention, is now in process of erection by the State. Carbon bisulphide has been used as a poison for this insect, but has been found to destroy the plants. Several of the American sorts of vine have been found to be free from the attacks of the phylloxera, and it is therefore recommended to plant only such kinds. *Vitis aestivalis* and *V. solonis* are mentioned

as being in Austria the only sorts capable of resisting the ravages of the phylloxera.

J. K. C.

Analytical Chemistry.

Dust in the Air. By G. TISSANDIER (*Bied. Centr.*, **10**, 131).—A measured volume of air was allowed to bubble slowly through distilled water, the latter evaporated, and the residue weighed. In this way 1 c.c. of air was found to contain:—

In Paris	{	After heavy rain	0.0060 gram
		„ 8 days of dry weather	0.0230 „
		Under normal conditions ..	0.0060 „
			0.0075 „
In the country ..	{	Under normal conditions ..	0.0080 „
			0.0025 „
		After lengthened drought ..	0.003 „
			0.0045 „

Pieces of paper were placed in inclined positions, and the dust which had settled on them collected after 24 hours; it weighed on different days 0.0021—0.001 gram. In one litre of rain-water 0.0250—0.1720 gram, in snow-water 0.048—0.212 gram was found. Atmospheric dust contains from 25 to 34 per cent. combustible, and from 75—66 per cent. incombustible matter. In the latter were found chlorides and sulphates of the alkalis and alkaline earths, ammonium nitrate, ferric oxide, calcium and magnesium carbonates, with traces of phosphates, silica, &c.

J. K. C.

Volumetric Determination of Peroxides. By A. TERREIL (*Bull. Soc. Chim.*, **35**, 551—552).—The author determines the oxidising power of peroxides by a standard solution of ferrous sulphate acidulated with sulphuric acid. The ferrous sulphate is titrated by a solution of potassium permanganate.

V. H. V.

Note.—This method has previously been adopted by Wright (this Journal, 1880, p. 44).—V. H. V.

Employment of Potassium Permanganate in Quantitative Analysis. By F. KESSLER (*Ber.*, **14**, 1258—1259).—A question of priority.

W. C. W.

Use of Oxalates in Analysis. By M. A. v. REIS (*Ber.*, **14**, 1172—1179).—Silver, lead, cadmium and bismuth may be precipitated by ammonium or potassium oxalates from neutral solutions or those containing free acetic acid. In the case of lead and bismuth the precipitates formed by potassium oxalate are double salts having the formulæ $\text{PbC}_2\text{O}_4 \cdot \text{K}_2\text{C}_2\text{O}_4 + 2\frac{1}{2}\text{H}_2\text{O}$ and $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4$ respectively.

The author proposes to determine these metals by this means, and further to separate copper from lead or silver by taking advantage of the solubility of copper oxalate in ammonium oxalate. The precipitates of lead, cadmium, and bismuth are ignited with ammonium nitrate and weighed as oxides, that of silver is moistened with strong nitric acid, ignited and weighed as metal. For further details the original should be consulted.

Estimation of Alumina.—When ammonium oxalate is added to a neutral solution of aluminium chloride or sulphate containing calcium chloride, the author has observed that the first precipitate of calcium oxalate disappears on standing, or more quickly if the solution is heated to boiling, and further that a permanent precipitate of calcium oxalate is not obtained until the amount of ammonium oxalate added is in the proportion of 3 mols. of ammonium oxalate for 1 mol. of alumina present. To make use of this observation in estimating alumina, the solution made alkaline with ammonia, and then acidified by acetic acid, is heated to boiling, and calcium chloride is added to it. To this is then added a titrated solution of ammonium oxalate until a permanent turbidity is obtained; and the amount of alumina calculated from the ammonium oxalate acquired. In presence of sulphates care must be taken not to add too much calcium chloride. Salts of iron and chromium have a somewhat similar effect on the precipitation of calcium salts by ammonium oxalate.

The properties of the oxalates of the iron and barium groups may be utilised in the qualitative examination of the precipitate produced by ammonium sulphide in presence of phosphoric acid, as follows. The solution of the portion soluble in dilute hydrochloric acid is evaporated to dryness, the residue dissolved in potassium oxalate with the aid of acetic acid. Twice its volume of acetic acid is added, and the solution boiled. By this means manganese, zinc, magnesium, calcium, strontium, and barium are precipitated. To the filtrate twice its volume of strong alcohol is now added to precipitate the oxalates of iron, chromium, uranium, and aluminium. The whole of the phosphoric acid is found in the filtrate from these. P. P. B.

Strength of Solutions of Sulphur in Carbon Bisulphide, and its Application to the Analysis of Sulphur Ores. By H. MACAGNO (*Chem. News*, 43, 192).—The specific gravities of several solutions of sulphur in carbon bisulphide, obtained at 15° with as much accuracy as possible by the specific gravity bottle, enabled the author to construct a curve representing the solubility of sulphur. This curve remains perfectly straight from 1.271 to 1.354 sp. gr. at 15°; from 1.354 to 1.390 it becomes scarcely curved towards the ordinate, on which the weights of sulphur are marked. The same happens at various temperatures from 15° to 25°. The curves result symmetrically arranged, and their curvature becomes more and more remarkable with the growth of temperature. By the method of graphical interpolation the author has calculated a table showing the quantity of sulphur in 100 parts by weight of carbon bisulphide.

15° C.	100 pts. of CS ₂	15° C.	100 pts. of CS ₂
Sp. gr.	dissolve	Sp. gr.	dissolve
1·271	0·0	1·340	16·6
1·280	2·1	1·350	19·0
1·290	4·6	1·360	21·8
1·300	7·0	1·370	25·1
1·310	9·4	1·380	30·2
1·320	11·8	1·390	36·7
1·330	14·2	1·391	37·2 (saturated)

In order to rapidly estimate sulphur in sulphur ores, the above table supplies a good and ready process to within a per cent. at least of sulphur in ores. We must know—

P = the weight of carbon bisulphide taken.

M = the weight of ore mixed with it.

A = the figure resulting from the table in order to see specific gravity of the solution of sulphur in carbon bisulphide at 15°.

Then the per cent., x , of sulphur in ore will be known by—

$$x = \frac{AP}{M}. \quad \text{— In the case of temperatures between 15° to 25°, as it}$$

generally may occur, the specific gravity observed may be reduced to its amount at 15° by means of the following formula, provided it be less than 1·352:—

$$S = s + 0\cdot0014(t - 15^\circ), \text{ where } S = \text{sp. gr. at } 15^\circ \text{ (that must be } < 1\cdot352); s = \text{sp. gr. observed at } t \text{ of temperature.} \quad \text{D. B.}$$

Action of Ammonium Citrate on Phosphates. By A. GRUPE and B. TOLLENS (*Ber.*, 14, 1042—1048).—A reply to the remarks of Herzfeld and Feuerlein (*Zeits. Anal. Chem.*, 20, 191) on the authors' paper on this subject (*Ber.*, 13, 1267, and 14, 754; this Journal, 1880, Abstr., 825). W. C. W.

Solubility of Tricalcium Phosphate in Ammoniacal and Neutral Alkali-salts. By A. TERREIL (*Bull. Soc. Chim.* [2], 35, 548—551).—In order to determine the chemical reaction whereby the earthy phosphates are introduced into vegetable organisms, the author has made a series of researches on the solubility of the phosphates in the alkaline salts of inorganic and organic acids.

The method of procedure was as follows. Pure gelatinous tricalcium phosphate was dissolved in a known weight of the acid, the solution neutralised with ammonia, the precipitate of calcium phosphate separated off, and the phosphoric acid left in solution determined by magnesium mixture. The following solubility coefficients were found for the ammoniacal salts of these acids:—

	Solubility coefficient.
Hydrochloric acid	0·655
Nitric „	0·309
Sulphuric „	1·050
Acetic „	0·255
Tartaric „	4·56
Citric „	7·00
Malic „	1·13

Calcium phosphate is also dissolved by potassium and sodium salts, but their solubility coefficient is far less than that of the corresponding ammonium salts. The author proposes to study the influence of organic substances on the solubility of calcium phosphate in neutral solutions. V. H. V.

Employment of Ammonium Citrate in Examination of Phosphates in Manure. By R. HERCHER and P. WAGNER (*Landw. Versuchs.-Stat.*, **27**, 1—14).—The method proposed by Petermann for the separation of phosphates of different solubilities appears to the authors likely to simplify the modes of procedure hitherto in use, as it precipitates the citric acid extract directly by magnesia mixture. If the results are found to be trustworthy, the process will be of great value, as it facilitates the estimation not only of the phosphates soluble in presence of citric acid and in water, but also of ferric and aluminic phosphates.

The authors had undertaken a thorough investigation of the process, when they learned that other persons had been already busy with the subject; they therefore publish the results of their experiments so far as they had gone, and declare them corroborative of the more detailed investigations of the other observers.

Twenty-two samples of superphosphates containing ferric phosphate, the soluble phosphoric acid in which ranged from 10 to 15 per cent. capable of precipitation by sodium acetate, and consequently not to be estimated, were treated first by the molybdic method in the usual way, 25 c.c. of the extract being employed. Duplicate samples were then operated on with ammonium citrate, viz., to 25 c.c. of the aqueous extract of the superphosphate were added 20 c.c. of a solution of neutral ammonium citrate of 1.09 sp. gr., 1 litre treated with 50 c.c. of 8 per cent. ammonia solution; 45 c.c. of 5 per cent. ammonia and 15 c.c. magnesia mixture were then added, left undisturbed for 15 hours, filtered, and the precipitate treated in the usual manner. The average of the 22 determinations agreed very closely, that by the molybdic being 15.83, and by citrate method 15.82 per cent.

The maximum difference between the two methods in the case of individual samples was 0.30 per cent., but the authors attribute this to the different composition of the superphosphates employed, and not to inexact manipulation or defects in the systems. To determine the amount of iron and alumina, nine experiments were made with some of the same samples. 200 c.c. of the superphosphate solution were decomposed with 50 c.c. of a 10 per cent. solution of sodium acetate, and 25 c.c. of the filtrate titrated with standard uranium acetate, 1 c.c. = 0.005 gram phosphoric acid.

Nine experiments were also made on chemically pure compounds of phosphoric acid with bases, viz., tricalcium, sodium, ferric, and ammonium phosphates, in order to test the relative values of both modes of estimation. With the first three the citrate method showed 3.1—1.0—0.3 mgrms. of phosphoric acid more than the molybdic, but in the case of the ammonium phosphate there was a deficiency of 0.7 mgrm. The authors conclude that when the phosphoric acid

exists in combination with a fixed body it is very liable to carry down with it into the precipitate a sensible amount of the body with which it is in combination. This appears to be particularly the case with calcium, which is probably precipitated as calcium citrate, but as the soluble phosphate in superphosphate contains but one-third of the calcium in the tribasic phosphate, the authors think it probable that the plus and minus errors balance each other, and that the citrate method might be usefully employed in the estimation of phosphates not otherwise determinable.

The authors investigate the subject further—whether the citrate method is a suitable one for separating phosphates of different degrees of solubility when they are found together in commercial artificial manures.

They describe Petermann's mode of procedure and experiments made with it. They recommend some modifications which they have adopted, viz.:—1 gram to 5 grams of the sample, according to its richness in phosphoric acid, are rubbed up with the ammonium citrate solution previously described, till 100 c.c. are employed, washed into a quarter liter flask, the mixture digested exactly one hour in the water-bath at 36° to 38° C., filled to the mark with distilled water, and filtered. To 50 c.c. of the filtrate are then added 25 c.c. of 8 per cent. ammonia solution and 15 c.c. of magnesia mixture, all the while stirring or shaking. The whole is then left at rest for about 15 hours, filtered, and the precipitate dried and ignited. The result of many experiments undertaken to compare the differential method of Fresenius and the citrate method, confirm them in their opinion that there is a satisfactory agreement between the two. The authors, however, believe that the quantity of phosphoric acid dissolved by the citrate solution varies with the nature of the phosphate; for example, the same quantity of citrate solution will dissolve a much larger proportion of the acid contained in precipitated phosphates than in phosphates made from phosphorite; the latter must always contain calcium sulphate, and the authors' explanation is that a certain quantity of the citrate is employed in saturating the gypsum, leaving less to act on the calcium phosphate. This view they confirm by other experiments, so that, as already shown, not only the proportions between phosphate and citrate, but also the composition of the sample as regards gypsum, exercise disturbing influences on the results. The concentration and reaction of the citrate solution, the state of division of the substance, the duration of the operation, the temperature, the frequency of stirring or shaking, the difference in the time of precipitation by the magnesia mixture, all influence the result, so that in the authors' opinion the citrate method cannot be strongly recommended as a control in manure analysis. They do not condemn it, but expect that improvements will be introduced which will reduce its inequalities to a minimum.

J. F.

Action of Ammonium Citrate on Phosphates. By C. ANTZ and E. ERLÉNMEYER (*Ber.*, 14, 1253—1255).—Experiments on the solubility of the trimetallic phosphates of calcium, magnesium, manganese, and iron in solutions of (1) diammonium citrate, sp. gr. 1.09, (2) triam-

monium citrate, sp. gr. 1.09, (3) triammonium citrate mixed with ammonia, and (4) a quarter per cent. solution of citric acid, show that the diammonium citrate is the most powerful solvent. 1 gram of the phosphate was treated with 400 c.c. of the citric acid solution at the ordinary temperature or with 100 c.c. of the citrate solutions at 38°. From the results of their experiments the authors recommend that in determinations of the amount of soluble phosphates in manures, the substances should be digested with citrate solutions for five hours instead of one hour. The temperature need not exceed 40°.

W. C. W.

Alkalimetry with Phenolphthaleïn as Indicator. By R. B. WARDER (*Chem. News*, 43, 228).—Luck seems to have been the first to use phenolphthaleïn as an indicator in alkalimetry. With caustic alkalis the delicacy of the reaction is marvellous; but when carbonates are present, the change of colour takes place more gradually, and cold solutions of an acid carbonate are not coloured at all. Even the carbonic acid of the atmosphere may have a marked influence. The following experiment was made: oxalic acid was added to a cold dilute solution of sodium carbonate, and the solution of HNaCO_3 produced treated with phthaleïn. No colour was obtained until the solution is decomposed by heat. It may be expected that the reddened solution of a carbonate would be entirely decolorised by half equivalent of acid. This, however, has been realised only in part, but it is thought that the facts indicated serve as a basis for a method for the estimation of causticity of solutions which do not contain too large a proportion of carbonate. The alkaline solution with a suitable quantity of phenolphthaleïn is mixed with standard acid in the cold, until the red colour either vanishes entirely, or (if the reaction is lacking in sharpness from the presence of carbonate) until the colour is extremely faint. The changes of tint closely resemble those observed when a solution of rosaniline is greatly diluted, and it is a valuable aid to the eye to keep such a solution at hand for comparison; and as the depth of colour at this stage varies with the quantity of indicator used, it is desirable to take some definite amount. After completing the first titration, the mixture is boiled thoroughly with successive additions of more acid, until the last returning trace of red colour is discharged by a single drop; or the end may be more quickly reached by boiling at once with excess of acid, and completing titration with the aid of caustic alkali. The end reaction in this case, which is very sharp, is marked by total discharge of colour.

The author is continuing this investigation with a view of ascertaining whether the method can be modified for the detection and estimation of carbonic acid in general.

D. B.

Estimation of Barium as Chromate. By H. N. MORSE (*Amer. Chem. J.*, 1880 [2], 176—181).—The author has examined the method proposed by Frerichs (*Ber.*, 1874, 800, 956) for the estimation of barium in presence of strontium, calcium, and magnesium, viz., by precipitating it from solutions containing acetic acid by means of potassium chromate, collecting the precipitate on a weighed filter, and washing

with dilute acetic acid. His experiments—which, however, he regards as merely preliminary—have led to the following conclusions:—

(1.) Barium can be precipitated, in presence of acetic acid, by an excess of potassium chromate, nearly, if not quite, as completely as by sulphuric acid. (2.) The precipitate cannot be washed with pure solutions of acetic acid, however dilute. (3.) If a small quantity of potassium chromate be added, the precipitate can be washed with quite concentrated solutions of acetic acid without undergoing solution. By using a wash-liquid containing potassium chromate, barium might perhaps be readily and completely separated from strontium, calcium, and magnesium. Any other soluble chromate would in all probability protect the barium-compound equally well. H. W.

Separation of Zinc from Cadmium. By KUPFFERSCHLÄGER (*Bull. Soc. Chim.* [2], 35, 594—595).—It has been observed that the electrolytic process for the separation of zinc from cadmium proposed by Riche and others is not exact, for the two metals are precipitated at the same time in proportions which vary according to the conditions of the experiments. The author has also observed that the separation is incomplete when a plate of magnesium is immersed in a mixed solution of the salts of the two metals. But if a plate of polished zinc be substituted for magnesium, the separation is exact, and requires but a short time for its completion. The author recommends that the solution be neutral, and previously boiled to expel the air, and that the assaying vessels be partially closed. V. H. V.

Quick Method for the Estimation of Lead. By ROUX (*Bull. Soc. Chim.* [2], 35, 596—597).—The gravimetric method for the determination of lead, though exact, yet requires too long a time for trade analysis; the author therefore proposes the following rapid process. The lead alloy (tin and lead) is dissolved in nitric acid, a saturated solution of sodium acetate is added to the solution, and the stannic acid allowed to settle. An aliquot part of the clear supernatant liquid is withdrawn, and the lead precipitated by an excess of a standard solution of potassium dichromate. The precipitate is separated off and washed, and the excess of dichromate determined by a standard solution of ammonio-ferrous sulphate, using potassium ferricyanide as an indicator. The lead must not be precipitated in presence of stannic acid, for portions of potassium dichromate solutions are mechanically retained by the precipitate. V. H. V.

Titration of Iron with Sodium Thiosulphate. By E. HASWELL (*Dingl. polyt. J.*, 240, 309—312).—For the volumetric determination of iron according to Oudemans' method, which has been slightly altered by the author, who uses salicylic acid as indicator, and potassium dichromate as oxidising agent, the following solutions are required. A solution of sodium thiosulphate standardised with iron solution; a solution of potassium dichromate to be about half as strong as the sodium thiosulphate solution; a solution of copper prepared by dissolving 2 grams of chloride of copper and ammonium free from

iron in 100 c.c. of water; and a dilute solution of sodium salicylate containing about 5 grams in 1 litre.

5 or 10 c.c. of the iron solution are measured into a small flask acidified with a few drops of hydrochloric acid, and treated with 1 to 2 c.c. copper solution and a few drops of sodium salicylate solution. If the colour is not a pure violet but olive-brown, the solution must be diluted with water. The sodium thiosulphate solution is then run in drop by drop from a burette until the solution is rendered colourless. The small excess of reducing agent is then titrated back with the potassium dichromate until the solution assumes a faint violet colour. For determinations which do not require absolute accuracy, the titration with potassium dichromate can be dispensed with, as two or three drops (equal to 0.1 to 0.15 c.c. sodium thiosulphate solution) suffice to obtain the end reaction. The author gives the results of a number of analyses made by this method, which appear to be very accurate.

D. B.

Determination of Ethylene and Benzene-vapour in Coal-gas. By O. KNUBLANCH (*Ber.*, **14**, 1163—1168).—The author has shown (*Ber.*, **14**, 240; this vol., 329) that half the illuminating power of gas measured with an hourly consumption of 170 litres, is equal to the number of grams of carbon which must be separated from the molecule of an organic compound to produce this illumination. Hence for illuminating power 18.5 9.25 grams of carbon must be separated, corresponding to 10.02 grams of benzene, or 1.69 per cent. in volumes of benzene-vapour. The same result would be attained with 10.14 per cent. in volume of ethylene, since the illuminating powers of equal volumes of ethylene and benzene are as 1 to 6. Hence with an hourly consumption of 100 litres of gas containing 1 per cent. in volume of benzene-vapour, the illuminating power would be 6.44, and with the same amount of ethylene it will be 1.0733.

With the aid of these data, and of the percentage of illuminants as given by absorption with concentrated sulphuric acid, and of the illuminating power calculated for a consumption of 100 litres, the amounts of ethylene and benzene-vapour are determined as follows:—

x = percentage in volume of benzene vapour
 y = " " ethylene
 S = " " illuminants
 L = candle power for 100 litre consumption, with
 a flame 45 mm. high.

Then $6.44x + 1.07337 = L$
 $x + y = S.$

Hence $x = \frac{1}{6} \left(\frac{L}{1.0733} - S \right)$ and $y = S - x.$

A table is appended illustrating the application of this method. In cases where the illuminating power is determined by other units, then L must be multiplied by a number greater or less than one, according as the unit is greater or less than the one described above.

P. P. B.

Sensitiveness of Trommer's Test; Fehling's Solution as a Qualitative Reagent for Sugar. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv*, **22**, 374).—Trommer's test is much more delicate at 60° than at ordinary temperatures, and it was found possible by means of it to detect 0.33 mgrm. sugar dissolved in 5 c.c. water. 3 mols. of cupric sulphate are required for 1 mol. of sugar, and 200—300 mols. of alkali at least must be present. At the boiling temperature 0.025 mgrm. of sugar could be detected in 1 c.c. of water; 30—100 mols. of alkali and 4 mols. of cupric sulphate suffice at this temperature for 1 mol. sugar. Fehling's solution was found to be still more delicate if freshly prepared, and the authors were able to detect 0.0083 mgrm. of sugar in 1 c.c. of water by means of it.

W. N.

Scheibler's Method of Estimating Sugar in Beet. By B. TOLLENS (*Bied. Centr.*, **10**, 121—126).—In order to fully test the capabilities of Scheibler's method, the author undertook to investigate the following points in connection with it:—whether the rotatory power of sugar is the same in aqueous and alcoholic solution; whether the filtration or the boiling of the alcoholic solution has any influence on the result, if the quantity taken was large enough, and the dilution of the sugar not too great, to cause considerable errors of experiment. All these questions received from the author's investigation a very satisfactory answer in favour of Scheibler's method; the experimental error was found not to exceed one-third per cent., and the results obtained by this method are much more trustworthy than those obtained by direct polarimetry of the sap.

J. K. C.

Value Constant for Beet. By F. KNAUER (*Bied. Cent.*, **10**, 126—127).—This constant, to express the value of a crop of sugar-beet, is obtained by dividing the sugar percentage obtained by Briss's saccharometer by the quantity of real sugar, and multiplying the quotient by the weight of yield per hectare.

J. K. C.

Determination of Fat in Milk. By S. P. SHARPLES (*Chem. News*, **43**, 228).—Five grams of the milk are evaporated in a flat platinum dish, the size being 65 mm. in diameter, and 15 mm. deep; 5 c.c. of milk form a layer over the bottom of this about 2 mm. thick, and when dry the layer is less than two-tenths of a millimeter thick. The film first formed on the surface settles in a honeycomb-like mass on the bottom of the dish. The drying will take about an hour and a half, and is best completed by heating for fifteen minutes in the oven at 105°. The dish after being weighed, is filled with light petroleum and left under a bell-glass for half an hour; the liquid is then poured off, taking care not to lose any of the upper film, and the dish refilled, this operation being twice repeated. The dish is then dried at 105° and again weighed; the loss gives the fat. The residue is ignited, and gives the ash. All stirring of the milk before it is dry must be carefully avoided. The following are duplicate analyses made by this method, the sugar being determined by titration. The milk in the second case was seized as adulterated:—

	No. I.		No. II.	
Volume per cent. cream..	18.0		6.0	
Sp. gr.	1.030		1.021	
Sugar	4.19	4.19	3.45	3.45
Casein and albumin ...	5.17	5.23	2.79	2.78
Ash	0.72	0.72	0.47	0.48
Solids not fat	10.08	10.14	6.71	6.71
Fat.....	4.35	4.35	2.31	2.31
Total solids	14.43	14.49	9.02	9.02

D. B.

Detection of Artificial Colouring Matters in Red Wines by means of the Spectroscope. By H. MACAGNO (*Chem. News*, 43, 202).—The author obtained, with several colouring matters commonly mixed with red wines, a series of very characteristic absorptions which were well defined, œnolin being driven away by special treatment hereafter mentioned.

Archil.—This substance is soluble in ethylic and acetic ethers, and when aniline colours are sought for in a wine by ordinary processes, one may be led into a great error. But the ethereal solution observed by the spectroscope gives absorptions which evidently show that aniline compounds are not the active agents here.

Hollyhock (*Althea rosea*).—When a wine containing hollyhock is treated with ammonium-alum and sodium carbonate, a violet liquid is obtained on filtration.

Portugal Berries (*Phytolacea*) and *cochineal* can be easily detected by potassium alum and sodium carbonate.

Bilberries (*Myrtille*).—This colouring matter is identical with œnolin.

Indigo.—A gelatin solution is mixed with wine; the precipitate formed is thrown on a filter and washed with water and alcohol; indigo passes through the filter and a blue colour appears in the washings. This liquid gives a characteristic absorption in the red. The following absorptions were obtained:—

Archil.	Hollyhock.	Portugal berries.	Cochineal.	Indigo.
5892 <	6550 <	5850 <	5850 <	6705 <
5700	6520	5625	5775	6550
∞	6325	5400	5667	6267
—	6150 <	5134 <	5562 <	5362 <
—	5225 <	—	5425 <	—
—	4860	—	5325	—
—	∞	—	5225	—
—	—	—	5134 <	—

In a paper "On the Detection of Aniline Colours in Wines," the author makes use of this means of representing absorptions.

D. B.

Technical Chemistry.

Poisoning by Choke-damp and Coal-gas. By R. BIEFEL and T. POLECK (*Dingl. polyt. J.*, **240**, 199—206).—In the authors' analyses the quantities of gas were measured in the moist state. The carbonic anhydride was absorbed in a wet potash-bulb, the oxygen in a bulb containing paper saturated with a concentrated alkaline solution of pyrogallic acid. In both cases the gas was completely dried by passing through a bulb of solid potassium hydroxide and measured. The analysis was then finished in the eudiometer, and in all cases the carbonic oxide was determined as carbonic anhydride by combustion in oxygen and addition of oxyhydrogen gas. In the analyses of common gas the heavy hydrocarbons were absorbed in a bulb filled with fuming sulphuric acid; carbonic oxide, hydrogen and lighter hydrocarbons by combustion analysis in the eudiometer. The air of a room in which a chafing dish had been exposed was analysed. It was found that the composition of the gas was characterised by the fact that in all cases the proportion of carbonic anhydride to the amount of oxygen is altered at the expense of the latter, and that the corresponding quantity of air is mixed with a changeable percentage of carbonic oxide. A weak rabbit died when 0.19 per cent. by volume of carbonic oxide was present; others required 0.3 per cent. With gas poisoning the conditions appear to be different. The air is not deprived of oxygen, and the proportion of the latter to the nitrogen remains normally about the same, as the composition of the air is not altered chemically, but merely by being expelled as the gas flows in. Carbonic oxide may be present to the amount of 0.5 per cent. in air containing illuminating gas before it acts fatally. The limits within which certain quantities of carbonic acid can be inhaled without proving fatal, appear to be larger with common gas poisoning than with choke-damp poisoning. When pure carbonic oxide was introduced in the air to be inhaled, 1.02 per cent. CO could be borne for a short time. The experiments with pure carbonic anhydride show that when 6.7 per cent. are present, the animal operated on became feeble, but quickly recovered in the air; however, with 50.4 per cent. death resulted.

The fatal action of sulphuretted hydrogen is important, inasmuch as its presence in illuminating gas and in the gases from mines and sewers, is a very frequent occurrence. Death follows after exposure to air contaminated with 0.05 per cent. in one hour twenty minutes, the symptoms being different from those of poisoning with choke-damp. The changes which coal-gas undergoes in its composition when it passes through layers of earth are of the utmost importance in toxicology. Gas was found to lose about 75 per cent. of the heavier hydrocarbons, and with them the vapours of tar ingredients had been condensed; these impart to gas its smell. Hence it was observed that the escaping gas had lost its characteristic smell almost entirely. A reduction of 50 per cent. in marsh-gas had been effected,

whilst the quantity of hydrogen remained the same, and that of carbonic anhydride had apparently increased 25 per cent. D. B.

Purification of Foul Water. By A. MÜLLER (*Bied. Centr.*, **10**, 132).—By the method described in this paper the decomposition of the putrefying matter by means of bacteria into simple inorganic compounds is encouraged as much as possible, the necessary food for the germs being provided, and the temperature being brought up to the most favourable point. In this way the author hopes to provide a rational and effective means of purifying all kinds of organic drainage.

J. K. C.

Chemical Technology of Alkalis. (*Dingl. polyt. J.*, **240**, 218—224 and 313—317.)—Mehner describes very minutely the recent progress made in the manufacture of salt, chiefly discussing the evaporation process and the construction of the evaporating pans. He gives the preference to the old square pans. Pans with mechanical means of agitation are said to give an impure product, Piccard's apparatus being the only one which gives a salt of peculiar fineness and great purity. The remaining portion of this part of the paper is devoted to descriptions of apparatus used in connection with the manufacture of salt at some of the principal salt works in Germany. It is pointed out that the drying operations are most profitably conducted on iron plates, utilising the waste heat from the evaporating pans. Mechanical appliances, *e.g.*, centrifugal machines, drying on hurdles, &c., have always been found too costly.

A new Potassium-magnesium Sulphate.—Hitherto the only salt of this kind known has been the compound $\text{K}_2\text{SO}_4, \text{MgSO}_4, 6\text{H}_2\text{O}$, called in mineralogy picromorite, and known in Stassfurt as schönite. By recrystallising this salt it is decomposed, and about one half of the difficultly soluble potassium sulphate separates, leaving in solution a new salt of the composition $\text{K}_2\text{SO}_4, 2\text{MgSO}_4$. Precht prepared this salt by decomposing kainite. The decomposition begins at a pressure of one atmosphere; on a large scale the pressure is increased to 2 to 4 atmospheres, corresponding with a temperature of 120 — 145° , a quicker and more perfect decomposition taking place. A saturated solution of salt is used, and the quantity regulated so that sodium chloride and the new double salt remain undissolved, whilst the potassium and magnesium chlorides are in the solution.

Napier and Tatlock found that hydrogen gas is evolved by the action of concentrated sulphuric acid on lead. The lead contained traces of copper and iron; otherwise it was very pure.

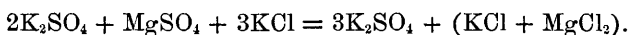
In order to convert the ammonium sulphide contained in gas liquor into ammonium sulphate, Young proposes to conduct the distillation products mixed with atmospheric air over a fire to condensation vessels. However, the sulphur when burnt forms sulphurous acid, and subsequently sulphuric acid, whilst the ammonia is destroyed.

Müller and Geisenberger describe the synthetical preparation of ammonia from the nitrogen contained in the air. Flue gases are freed from carbonic acid by means of lime; hydrogen is passed over red-hot coke; and the gas obtained is united with the nitrogen by being brought into contact with the electric spark. Ammonia is produced.

Basset ignites coke saturated with boracic acid in a retort covered with a layer of magnesia, lime, oxide of manganese, &c., and passes nitrogen over the mixture. When sufficient nitride of boron has been formed, hydrogen is introduced, and the ammonia produced is carried off and collected.

D. B.

Preparation of Potassium Sulphate from the Salts of the Stassfurth Deposits. By H. GRÜNEBERG (*Ber.*, 14, 1179—1183).—This is an account of the methods employed to utilise for the preparation of potassium sulphate from Stassfurth salts. The observations show (1) that the double salt, $K_2SO_4MgSO_4 + 6H_2O$, may be obtained by crystallisation from a mixture of 1 equivalent of potassium chloride and 2 equivalents of magnesium sulphate; and (2) that potassium sulphate may be obtained by decomposing this double salt with potassium chloride, thus:—



A short account is also given of the more important patents which have been taken out since 1877 for the preparation of potassium sulphate from the Stassfurth salts.

P. P. B.

Thiocarbonates of Potassium and other Metals. By VINCENT (*Ann. Chim. Phys.* [5], 22, 544—551).—The author alludes at the outset to the practical application of the thiocarbonates for the destruction of the phylloxera, and to the various commercial methods proposed for the preparation of these salts. These processes are separable into two distinct stages. 1st. The formation of the alkaline monosulphide; 2nd, the treatment of this product with carbon bisulphide. The preparation of the alkaline salt presents certain difficulties, and the commercial products are often not only unsatisfactory, but even in some cases injurious. The first method proposed for the formation of potassium monosulphide consists in saturating potassium hydroxide with sulphuretted hydrogen and conversion of the hydrosulphide formed into monosulphide by addition of the same weight of potassium hydroxide as that originally used. The product, although perfectly pure, is too costly for industrial purposes.

The second method consists in reducing potassium sulphate by carbon at a high temperature; but the alkaline sulphide obtained is readily oxidised in the air, with formation of polysulphides and sulphates, and the product is often contaminated with impurities derived from the apparatus used. In the third method proposed by the authors, barium sulphate is reduced by carbon in closed vessels, and the barium sulphide formed is dissolved in water, and decomposed by the requisite quantity of potassium sulphate. The sulphide is then converted into the thiocarbonate by agitating a slightly warmed mixture of a concentrated solution of the sulphide with carbon bisulphide. It is found necessary to fit the apparatus in which this change is carried on with an inverted condenser, in order to condense the carbon bisulphide which distils off, owing to the heat evolved during the

reaction. The solution of potassium thiocarbonate (containing about 13 per cent. of carbon bisulphide) is of an orange-red colour.

As it is most important for the wine grower to know the percentage of carbon bisulphide present in the sample, the authors recommend the method of analysis proposed by Delachanal, which consists in distilling the carbon bisulphide into an alcoholic solution of potash, and determining the amount of potassium xanthate formed by means of a standard iodine solution. A table is added in which is indicated the percentage of carbon bisulphide in solutions of potassium thiocarbonate of various densities.

It has been proposed to substitute sodium for potassium thiocarbonate, as the manufacture of the former salt presents no difficulties, and the cost is less; but the sodium salt is not so valuable as an insecticide, and it does not contain the potash, which serves as a manure for the vines.

V. H. V.

Occurrence of Arsenic and Vanadium in Commercial Caustic Soda. By E. DONATH (*Dingl. polyt. J.*, 240, 318).—As caustic soda is no longer prepared exclusively from raw soda and lime, but also directly from the "red liquors" of soda works, the constitution of commercial preparations is occasionally affected. Thus the author found that not only is the amount of chlorides and sulphates increased, but the presence of nitrites, cyanides, &c., has been observed. The author has recently found arsenic and vanadium in samples of caustic soda, to the amount of 0.16 per cent. of arsenic acid, and 0.16 per cent. vanadic acid.

D. B.

Steel for the Manufacture of Dies. By W. C. ROBERTS (*Chem. News*, 43, 239).—The following are analyses of typical samples of steel employed in the mint for dies:—

	A.	B.	C.	D.
Iron.....	98.93	98.63	98.64 (by diff.)	98.07
Carbon	0.82	1.07	0.79	1.19
Manganese....	0.10	0.12	0.24	0.45
Silicon.....	0.05	0.06	0.18	0.29
Sulphur	trace	trace	0.01	trace
Phosphorus....	—	trace	0.01	trace
Copper	—	—	0.02	—

The sample marked A was a die of exceptional quality, having struck no fewer than 200,000 florins, the normal out-turn of a florin die not exceeding 50,000 pieces. B is the steel now employed, which during the past year has been found to yield an average out-turn of 54,000 pieces per pair of dies. C proved in practice to be unsatisfactory, owing to the frequency with which it cracks during the operation of hardening, and this fault was still more marked in the sample D. Its use has therefore been discontinued.

The author undertook a complete series of investigations with the view of ascertaining which of the three varieties of steel (B, C, and D) would, with treatment in every way suitable to it, produce the

most perfect die. It is unfortunate that the sample A which struck 200,000 florins, being a finished die, could not be tested mechanically; the chemical analysis, however, indicates that it would stand cold water hardening even better than B. There can be no doubt that plunging red hot steel into cold water severely strains the metal, and the investigations generally show the special importance of studying the influence of hardening in the manufacture of dies. D. B.

A Pure Coke. By W. W. STAVELEY (*Chem. News*, **43**, 228).—The author has tested a sample of coke made from coal-tar pitch, and found it to contain a very small percentage of sulphur. The following is its analysis:—

Sulphur.	Ash.	Carbon by difference.	
0.12	2.43	97.45	
0.11	2.50	97.39	D. B.

Prevention of the Occurrence of Lactic Acid in Beer. By JÄCKEL-HANDWERK (*Bied. Centr.*, **10**, 142).—The barley must be free from dust, and the temperature of the mash, length of time of fermentation, cleanliness of apparatus, &c., be carefully preserved, the cooling of the wort being effected as quickly as possible. J. K. C.

Preparation of Braga-beer. By C. O. CECHE (*Dingl. polyt. J.*, **240**, 235—237).—The preparation of this beer in Russia is still carried on in its most primitive form. In order to obtain 25 wedros (at 12.299 litres) of beer, 1 kul (sack of corn) malt, 1 pud (40 pounds) shot-malt, 3 pounds (at 409.5 grams) cultivated garden hops, or 5 pounds wild or forest hops, and 40 wedros of water are taken. The whole of the malt is brought into a wooden vat, 1 pud of shot-malt added, and the mixture treated with 30 wedros of boiling water. In the meantime the hops are boiled in a boiler. In a second vat a layer of straw is spread over the bottom, the latter being provided with a small opening into which a long rod is fixed which is used as a stop-valve. The steamed hops are then brought into this vat, and the syrupy wort and boiling water added. The rod is then drawn up, and the hopped wort filters through the straw into a tub. It is again warmed, then brought in contact with the hops and filtered, and this operation is repeated till a thin liquid of aromatic smell has been obtained. 1 litre of yeast diluted with 4 wedros of hot water is now added to the wort, and the whole allowed to ferment for two hours. The beer is then transferred to casks, and left to ferment in a cool place, the yeast escaping through the vent-hole. After two or three days the vent peg is fastened firmly into the cask, and the beer is ready for use shortly after this time, but it is preferable to bury the casks in hay for a short interval. By this treatment the quality and clearness of the beer are considerably improved. D. B.

Creaming of Milk by Surface Cooling. By M. SCHRODT and v. PLOTHO (*Bied. Centr.*, **10**, 116—118).—The Tremser apparatus for the creaming of milk accomplishes its end by means of a surface cool-

ing of the milk with ice-cold water, precautions being taken that the quantity of ice required may be as small as possible. By this means a yield of cream is obtained nearly as large as that got by using Swart's apparatus. Experiments showed that when the water was not ice-cold, quite as large a yield was obtainable as by Swart's process, and there seems therefore to be no advantage in using ice, as the surface particles of the cream are rendered much heavier, and a constant commotion is thereby kept up in the liquid. J. K. C.

Preparation of Soap. (*Dingl. polyt. J.*, 240, 155—158).—According to a recent communication by Reul, "fine white hard soap" (also white soft soap, and toilet or glycerin soap) was first prepared by Grodhaus in 1843 from white tallow and cocoanut-oil. The tallow (500 kilos.) is treated with soda-lye of 10° B., and when the so-called corn or grain has been formed, a mixture of cocoanut-oil (150 kilos.) and soda-lye of 20° B. is added, and the whole treated with salt water of 20° B.

According to Reul, 300 kilos. tallow are saponified with soda-lye of 14° B., and then treated with 150 kilos. cocoanut-oil or palm-oil. The mass is treated with soda-lye of 25° B., then salted out and clarified. The clear mass is then transferred to a second vessel, which has been previously heated with soda-lye of 25° B., and treated with 50 kilos. cocoanut-oil or palm-oil. It is saponified by gently heating the mixture, and as soon as the white soap has been dissolved in the slimy mass, the finished product will be deposited on the surface. According to a third method, 100 kilos. tallow, 100 kilos. white olein or melted fat, and 50 kilos. cotton seed-oil are saponified with soda-lye of 14° B., and when the slime is clear, 25 kilos. cocoanut-oil or palm-oil are added and finished off with soda-lye of 25° B. with the addition of about 10 kilos. salt. The next operation is the salting out, then the clarification by means of heating, and finally the addition of water.

Deite mentions that saponification in the cold is a very convenient means of preparing soap; but although the plant used is simple in construction and the capital required is small, this method of preparation demands pure raw materials. It is applicable only to cocoanut-oil or to mixtures of the latter with other fats. D. B.

New Process for Extracting Tannin by Dialysis. By O. KOHLRAUSCH (*Dingl. polyt. J.*, 240, 72—75).—Some time ago it was proposed to prepare tannin extracts in Hungary, from a variety of barks and woods, especially chestnut wood and oak. The author has thoroughly investigated this question, and succeeded in devising a process of extracting tannin in almost theoretical quantities from different kinds of bark. The mode of procedure, necessary apparatus, and plant are described in detail. With regard to the experimental part of the paper, the author concludes that as in tanning the tannin enters the skin by osmosis, it similarly leaves the cells of plants through their permeable membrane, chemical and microscopical examination having shown that the interior of the uninjured cells is the same as the exterior of thick bark which had already been utilised. It is therefore not the solution of the tannin set free by finely dividing

the bark, and taken up by the skins, but dialysis of the tannin through the permeable membrane of the plant cells, and also through the animal membrane of the skin. Hence it is not requisite to divide the bark into very small particles, but pieces may be used with advantage which are small enough to allow the dialysing operation to take place in a battery of closed vessels, thus avoiding any danger of choking up the valves or pipes of the apparatus. The result is that purer extracts are obtained in a more economical manner, so that lighter-coloured leather is produced; and if the freshly-prepared extracts are used at once, the author believes that considerably less of the tannin in a fresh active state will be required for tanning. Experiments have shown that tannin passes through the animal membrane very rapidly in the dialyser; that in a short interval fine extracts run from a battery; and that the residual bark (of the size of peas) is almost entirely free from tannic acid. D. B.

Preparation of Leather. By W. EITNER (*Dingl. polyt. J.*, 240, 66—72).—Calcined Glauber salt is recommended for the preservation of raw hides.

With regard to the application of train oils in tanning, it is mentioned that a light-coloured oil deposits solid fat more readily than dark oils, that old oils are better than new, and that seal and whale oils have been successfully used in tanning when previously heated. This is said to effect a partial conversion and separation of the foreign fat. The following are the most important train oils of mammals found in commerce: Common whale oil, prepared from the Greenland whale (*Balaena mysticetus*), is mostly brought into commerce in the form of a light-coloured oil (called white train oil). Darker varieties, although less frequent, are found in commerce. Sperm oil (from *Catodon macrocephalus*) has a pale orange-yellow colour, is transparent, gives needle-shaped crystals at $+ 8^{\circ}$; has a sp. gr. of 0.884, and can be used only in small quantities for leather oiling, otherwise the leather will become stained. Dolphin oil is chiefly produced from *Globicephalus melas*, occurring in the north of Europe. It has a lemon-yellow colour, strong smell, is very mobile, and solidifies at $+ 3^{\circ}$ with separation of fatty crystals (cetin). This oil is most suitable for chamois-leathers. Seal oil is obtained from the fat of the various species of the family of seals of different seas, such as ear-seals (*Otaria*), common seals (*Phoca*), and walruses (*Trichechus*). These oils are more valuable than whale oil for leather, as they have a higher sp. gr., and hence add to the weight of leather. In the chamois-process, whale oil is transformed into a dark reddish-brown thick oil (Moëllon, pure French *dégras*), which no longer has the property of drying in the air. It forms a valuable oil for application to leather. Cod-liver oil forms the chief representative of fish oils, and is obtained from the liver of *Gadus morrhua*. Before use it is necessary to heat it, as in the case of whale and seal oils. A thick oil of strong sea-fish smell and taste, having a sp. gr. of 0.927, is obtained from herrings (*Clupidae*). The oil has an orange-yellow colour, remains liquid at 0° for some time, and then deposits a solid fat. Ray-liver oil, obtained from the livers of *Trigon pastinaca*, *Raja giorna*, and *Raja clavata*,

resembles cod-liver oil in most of its properties. Shark oil, obtained from the liver of sharks, has not yet been utilised in tanning. On the east coast of North America, a fish oil is obtained from the liver of the lamprey (*Petromyzon maximum*). This oil is used in America. The liver of the tunny (*Thynnus vulgaris*) yields an oil which gives as favourable a result when applied to leather as seal oil. The colour is yellowish-brown, sp. gr. 0.9275; its smell resembles that of sardines; it is a thick oil, and solidifies below 0°.

The author mentions that only the liquid portion of the fat in leather grease enters the leather, while the solid constituent, stearin, either remains outside on the surface, or if it penetrates into the leather, aided by mechanical means, it shows white stains on the leather.

It is stated that the problem of preparing a fine, uniform, well-covered light-grey colour, suitable for dyeing kid, is one of the most difficult tasks. The author, after a prolonged study, succeeded in obtaining a mixture which he recommends. It is composed of the following constituents:—2.5 kilos. of alder-bark are boiled out with 25 litres of water, finally the mixture is made up to 25 litres; 300 grams of fustic are boiled in 3 litres of water, and made up to 3 litres; 150 grams of logwood are boiled with 1.5 litres and made up to 1.5 litres; these are mixed together, diluted with 30 litres of water, and finally the mixture is treated with "ligustrum-juice." Four coats of this mixture are required. A solution of 1 kilo. ferrous sulphate in 600 litres of water is then applied.

The author gives a formula for preparing a solution said to impart to leather a fine lustre. It is composed of shellac, soap (Marseilles), and glycerol, and coloured black with nigrosin.

D. B.

Applications of Salicylic Acid. By SCHLUMBERGER (*Compt. rend.*, 92, 1042—1044).—Salicylic acid is a powerful antiseptic, and even when employed in infinitesimal quantities arrests the action of ferments. It is largely used as a disinfectant. A solution of 2 grams per litre is sufficient to destroy all disease germs, and remove all contagion. As a disinfectant for cattle trucks, it is far preferable to carbolic acid, as it leaves no smell. It is employed by veterinary surgeons as a curative for certain diseases of animals. It is also useful in preventing the spread of epidemics among animals. Its most important use, however, is the preservation of food. During the heat of summer, meat, game, and fish can be preserved with it for several days. The acid appears to act on the lactic and acetic ferment in preference to the alcoholic, which fact allows of its application to the preservation of alcoholic liquors. It is largely employed in preserving beers and wines.

J. I. W.

General and Physical Chemistry.

Experimental Determination of the Velocity of White and Coloured Light. By J. YOUNG and G. FORBES (*Chem. News*, **43**, 249).—The apparatus employed in this research to measure the velocity of light consisted of a revolving toothed wheel, used as in Cornu's method, to alter the intensity of the light reflected from a distance. Two distant reflectors separated by a quarter of a mile are used, the observing telescope and the two reflectors being almost in the same line. Two stars of light are visible, which go through their phases with different periods as the toothed wheel revolves at increasing speeds, one star increasing, while the other is diminishing in intensity, with increase of speed of the toothed wheel. The speed required to produce equality of light is determined by means of a chronograph. The final result for the velocity of the light from an electric lamp in a vacuum was found to be 187,273 miles per second.

The general conclusions of the paper are that the results seem to support the view that the more refrangible the source of light, the greater is the velocity, the evidence of the present observations indicating an excess of velocity for blue over red light, seeming to exceed 1 per cent. of the whole. D. B.

Spectrum of Carbonic Anhydride. By C. WESENDONCK (*Chem. News*, **44**, 42).—The well known spectrum, first observed by Swan at the inner cone of a number of flames produced by burning liquid and gaseous combinations of carbon, has been ascribed by Attfield and Watts to the element carbon itself; while Thalén, Ångström, Smyth, Liveing, Dewar, and others believe it to be due to some combination of carbon with hydrogen. The fact that the bands and lines of Swan's spectrum are seen even when carbonic oxide or anhydride is made luminous in a Geissler tube by means of an electric current, is explained as being caused by the gases not having been entirely deprived of moisture when introduced into the vacuum tube. The author therefore made some experiments on carbonic anhydride, dried with the utmost care. A mercurial pump, as invented by Toepler, was used, and carbonic anhydride prepared from marble and dilute hydrochloric acid in a Pippian apparatus, the gas being well washed with water, then sent through concentrated sulphuric acid, three tubes containing calcium chloride, and finally through a double tube half filled with phosphoric anhydride. The apparatus was then exhausted to the highest possible degree; nevertheless the green hydrogen line was seen with great constancy, and it was noticed that the more the gas had been deprived of moisture, the further had the exhaustion to be carried on to render the said line visible again, but for a long time it could not be got rid of entirely. The author eventually succeeded, after a great deal of trouble, in obtaining the gas so dry that it no longer gave any trace of the green line; but even in this case the bands and lines of Swan's spectrum were distinctly visible, a cir-

cumstance which is decisive in proving that Swan's spectrum cannot be ascribed solely to hydrocarbon. It is further demonstrated that there exists some relation between the different orders and forms of spectra and the conditions of discharge, probably the quantities of electricity sent through the unit of space in the unit of time—hitherto unknown to us, and which will doubtless be understood more readily as soon as the causes governing spark discharges shall be better recognised—a subject on which Thomson says that it is difficult even to conjecture an explanation.

D. B.

Spectrum of Sodium. By W. DE W. ABNEY (*Chem. News*, **44**,*3).—On examining the spectra of different metals, there is one point which is striking in the extreme, viz., the absence of any very marked lines in the region between λ 7000 and λ 7600, which latter number may be taken as the visible limit of the spectrum. It would appear that only those metals which can be volatilised at a low temperature have any lines in the ultra-red: sodium is an example of this. It has a pair of lines at wave-length of about 8187 and 8199 of an intensity of about 3, taking the intensity of D lines as 10. In the calcium spectrum there is a pair of very faint lines which lie between λ 8500 and 8600; their exact wave-lengths have not at present been determined. Iron, cobalt, nickel, copper, magnesium, and potassium have, up to the present, given negative results, but will be examined again.

D. B.

Alteration of Molecular Weight and Molecular Refractive Power. By J. V. JANOVSKY (*Wien. Akad. Ber.* [2], **82**, 147—158).—The author gives a large number of determinations of the indices of refraction of various bodies, and infers from a consideration of these determinations, that:—

1. The refractive power of the carbon compounds is dependent on the number as well as on the position of the atoms.
2. Isomeric bodies have different indices of refraction.
3. The index of refraction, and also the refraction equivalent of the elements (in their compounds) is variable, and dependent on the quality and quantity of the atoms present in the molecule.
4. In homologous series the value of the difference of the indices of refraction changes, and depends on the capacity of saturation of the hydrocarbons.

Saturated compounds of the hydrocarbons, C_nH_{2n+2} , show a positive—the hydrocarbons, C_nH_{2n-6} , a negative difference on addition of carbon and hydrogen.

The index of refraction of one and the same body is different in the solid and in the dissolved state: hence it is no longer allowable to calculate the index of refraction of a body from the indices of refraction of its solutions. Whilst the index of refraction of the derivatives of the hydrocarbons C_nH_{2n+2} increases on addition of CH_2 , the reverse is the case with the iodides, methyl iodide having a greater index of refraction than ethyl, and still more than amyl iodide.

F. L. T.

Action of Light on Silver Bromide. By G. NOEL (*Compt. rend.*, **92**, 1108—1109).—It is well known that when silver bromide is

exposed to the action of light for a short time it undergoes a molecular change, which is not apparent until the bromide is treated with some reducing agent. The author has found that when plates which have been exposed to light are kept in the dark for several months, they give no reaction with reducing agents, but behave just as if freshly prepared. Such plates, when again exposed, give as good an image as fresh plates. He finds that plates covered with silver bromide in emulsion in collodion lose all traces of the impression at the end of two months. Silver bromide produced by dipping a bromodised collodion film into a solution of silver nitrate, after exposure, retains its power of giving an image with reducing agents for a little more than five months; gelatino-bromide of silver gives an image which is very faint, but shows the principal details at the end of seven months. It would appear from these results that the more sensitive the silver bromide, the longer does it retain the peculiar molecular condition produced by the action of light, and that when this peculiar condition has disappeared, the bromide recovers its original sensitiveness.

C. H. B.

Action of Light on Phosphorescent Bodies. By CLÉMANDOT and others (*Compt. rend.*, 92, 1107—1108).—Young has found that the power of the blue rays to excite phosphorescence is much greater than that of the red, yellow, or green rays. Pleasonton has found that pigs fatten most rapidly under the influence of blue rays. These results confirm Clémantot's supposition that there is an analogy between the action of light on phosphorescent compounds and its action on organised bodies.

Becquerel showed some years ago that phosphorescence is a purely physical phenomenon, and that the refrangibility of the exciting ray depends on the nature of the phosphorescent substance. Alumina and Iceland spar, for example, are excited by the rays between D and F, whilst blende, and the majority of the sulphides of calcium, barium, and strontium are mainly excited by rays more refrangible than F.

C. H. B.

Curious Actinic Phenomenon. By T. L. PHIPSON (*Chem. News*, 43, 283).—The phenomenon in question was first noticed by T. Griffiths. The first observation was that a gate-post, painted white by means of a new white pigment, having a zinc basis, appeared black all day and white all night, turning black again soon after sunrise. The white pigment was prepared by precipitating a solution of zinc sulphate with a solution of barium sulphide, giving on analysis—

Loss by calcination	1.62
Barium sulphate	41.50
Barium sulphide	1.02
Ferrous oxide.....	2.12
Zinc oxide	16.30
Zinc sulphide.....	37.44
Lead, arsenic, manganese, &c.	traces.

The phenomenon is due to the use of barium sulphide in the preparation of the pigment, for specimens made by another process in

which barium sulphide was not used, did not show it all. It was also found that the white pigment did not darken when exposed to the sun, having previously been covered with a sheet of ordinary window-glass.

Cawley (*Chem. News*, **44**, 51) criticises the author's results. In order to make his remarks more intelligible, he gives the following description of the method generally adopted in manufacturing pigments containing sulphide of zinc. A solution of zinc salt, carefully freed from iron, manganese, &c., is precipitated by means of a solution of an alkaline or alkaline-earthly sulphide. The resulting precipitate is dried and ignited at a full red heat, thrown into water, and afterwards levigated, filtered, dried, and ground. The author states that the sample analysed by him was white; Cawley, however, finds that a pigment containing over 2 per cent. of protoxide of iron would be more nearly black. He cannot understand how barium sulphide and ferrous oxide could exist side by side in prolonged contact with water without any blackening taking place, and how barium sulphide could occur in the finished product; in other words, how barium sulphide can remain in prolonged contact with a hot solution of a zinc salt without being destroyed. In the manufacture, care is always taken to have a slight excess of zinc salt. The author is of opinion that the discoloration is connected with the presence of barium sulphide in the pigment; Cawley found that the pigment may be just as sensitive to light if no barium salt is used. Under a given set of atmospheric conditions he finds that a sheet of glass exerts no sensible protective action, whilst the author claims that such protection was complete.

D. B.

Production of Electricity by Contact of Heterogeneous Metals. By F. EXNER (*Wien. Akad. Ber.* [2], **80**, 307—327).—The author points out that the electromotive series of metals in air is the same as that of their oxidisability, and shows that the electromotive force of any two metals in air is measured by their heats of combustion. In a battery cell, as is well known, a certain chemical action produces a difference of potential proportional to its heat-equivalent; in the case of the oxidation of a metal in air, it must be said that the difference of potential between the metal and the resulting oxide is proportional to the heat of combustion of the former. Any insulated metal, when oxidised in the air, gives rise to positive and negative electricity, the observed potential being always constant whether oxidation progresses or not, the electricities reuniting as produced with evolution of the equivalent amount of heat; *e.g.*, if a piece of zinc has received from oxidation in the air the potential $+E$, and the layer of oxide (or possibly the adjacent layer of air) the potential $-E$, so that the difference of potential $= 2E$, then the amount $2E$ is measured by the heat of combustion of the zinc. If the zinc is connected with any metal not oxidised by air, *e.g.*, platinum, then a portion of the electricity of the zinc will flow over into the platinum until both metals have a common potential, *e.g.*, $+P$. The potential of the zinc will now equal $-E + P$, that of the platinum $+P$, so that the difference of potential between zinc and platinum is $-E$, and is measured by half the heat of combustion of the zinc. Let the heat equivalent of a Daniell $= A$ (calculated on chemical equivalent

lents of the substance), the heat of combustion of zinc = B, then the difference of potential between zinc and platinum in air must = $\frac{B}{2A}$.

If the metal connected with the zinc is also oxidised by the air, the same result would be obtained: the difference of potential between two metals is always measured by half the difference of their heats of combustion.

In order to prove the truth of the chemical theory, the author compares the observed differences of potential determined by Kohlrausch's method with the heats of combustion so accurately determined by J. Thomsen. A condenser was employed, consisting of the two metals under consideration, separated by a layer of paraffin; these were joined to the poles of a Daniell's cell, first in one direction, then in the other, the differences of potential being measured by a Branly's quadrant electrometer charged by a Zamboni's pile, the two plates being finally directly connected with the electrometer to check the results. The mean of 13 experiments between zinc and platinum gave 0.881 as their difference of potential, the Daniell being taken as unity, whilst the result obtained by calculation from the formula $\frac{B}{2A}$ was as follows:—

Heat of oxidation of zinc = 42700 (J. Thomsen).

Heat equivalent of Daniell = 24300 (J. Thomsen).

Hence the value of $\text{Zn} \mid \text{Pt} = 0.879$ Daniell. Using precisely the same method with copper and platinum, the author found by experiment $\text{Cu} \mid \text{Pt} = 0.367$ Daniell, by calculation, $\text{Cu} \mid \text{Pt} = 0.383$ Daniell.

Similarly, $\text{Fe} \mid \text{Pt} = 0.704$ Daniell (experiment).

„ = 0.701 „ (calculation).

$\text{Ag} \mid \text{Pt} = 0.083$ „ (experiment).

„ = 0.062 „ (calculation).

In the case of silver and platinum, the absolute numbers are so small that experimental errors prevent great accuracy; the experiment was undertaken merely to compare silver in air with silver in chlorine. The author prepared a condenser as above with two silver plates, and found naturally that in air there was no difference of potential, but on exposing the one plate to a current of chlorine, the other remaining in air, he obtained a difference varying from 0.57—0.50; theory, using Thomsen's numbers, demanding 0.543.

The only metal the author had any difficulty with was lead, which he attributes to its rapidly forming a coating of oxide on exposure to air, and to its inability to take a good polish.

While the above experiments were in progress, two papers by Brown (*Phil. Mag.*, 5, 6th August, 1878, and 7th February, 1879), bearing somewhat on the same subject, appeared. Brown concluded from a study of Volta's pile that the so-called contact-electricity owes its origin to chemical action which the surrounding gases exert on the metals. He

made the two halves of a Thomson's ring-electrometer of different metals and placed it in different gases; he found, *e.g.*, that with a copper-nickel couple, the copper was negative to the nickel in air, but positive to it in hydrochloric acid.

The author considers that although Brown has the priority in the qualitative exposition of the idea, still he (the author) was the first to prove the matter quantitatively.

F. L. T.

Theory of Inconstant Galvanic Cells. By F. EXNER (*Wien. Akad. Ber.* [2], **80**, 1055—1073).—In calling two-fluid batteries (Daniell, Grove, Bunsen) constant, and one-fluid batteries (Smee, Volta) inconstant, the expressions constant and inconstant apply naturally only to the electromotive force and not to the resistance; if a Daniell's cell remains closed for a time, the initial value of its electromotive force is not materially altered, but if a Smee's cell be similarly treated, a considerable diminution will take place in this value. This difference between the two cells is now universally attributed to galvanic polarisation, which is said to occur only in the latter cell; for whilst in the Daniell the hydrogen liberated by the oxidation of the zinc is utilised in depositing copper, in the Smee it is itself deposited as a film on the platinum plate, for it has hitherto been universally accepted that the cause of the polarisation is the contact of the metal (*e.g.*, platinum) with hydrogen. The author considers such an explanation to be untenable, especially as such a polarisation does not in general occur in galvanic cells. The author has shown (*Wien. Akad. Ber.*, **78**, and *Wied. Ann.*, **6**) that no electromotive excitation of metals occurs by contact with gases; he further showed that the polarisation in any decomposing apparatus has its origin in the recombination of the separated ions, and reproduction of the decomposed electrolyte, the electrodes themselves undergoing no chemical change, but merely acting as conductors of the electricity. The electromotive force of the polarisation, in the same manner as the electromotive force of a cell, is measured by the heat-equivalent corresponding with the chemical processes which occur.

It is obvious that, according to this theory, there are two cases where the decomposition of an electrolyte can occur without simultaneous polarisation: firstly, when for any reason the electrolyte cannot be reproduced from the separated ions, and, secondly, when such a reproduction has a heat-equivalent equal to zero. The first case occurs, *e.g.*, in the electrolysis of water with zinc electrodes; a reproduction of the water is impossible, as the separated hydrogen has not the power to turn the zinc out of its combination with the oxygen: polarisation therefore does not occur. The second case happens when a salt is decomposed by electrodes of the metal in question, *e.g.*, cupric sulphate by copper electrodes. The heat-equivalent of the reproduction of the electrolyte is equal to zero, so also the polarisation. The author proposes to consider a polarisable cell, *e.g.*, a Smee, firstly, from this point of view, and then from the point of view of the contact theory.

The electromotive force of a Smee can be compared with that of

a Daniell in the following manner, taking J. Thomsen's calorific values. In a Daniell, for each equivalent of zinc consumed 24,300 heat units are available. In a Smee, an equal consumption of zinc obviously renders much less heat (*i.e.*, electromotive force) available; for one equivalent of hydrogen is liberated for each equivalent of zinc consumed, therefore one equivalent of water is decomposed. From the consumption of the one equivalent of zinc in the Smee, we therefore only obtain 17,800 heat-units. Taking the electromotive force of the Daniell as unity, we have $S = 0.732$. This number may, for brevity, be called the "theoretical" electromotive force, in contradistinction to that actually observed.

According to the author's theory, no polarisation can occur in such a battery, and, furthermore, the electromotive force will not be altered by substituting another metal (*e.g.*, copper, as in Volta's cell) for the platinum, so long as the same chemical actions take place. On the contact theory, the chemical action must be taken as a measure of the electromotive force, so as not to contradict the conservation of energy. Therefore, even according to the contact theory, the electromotive force of the Smee is equal to 0.732 D.; but since a film of hydrogen on the platinum gives rise to polarisation, a smaller electromotive force must result: in other words, a Smee just put together must have a force of 0.732 D, which, on closing, rapidly sinks to a lower undetermined value.

In practice, it is found that there is a rapid falling off in the electromotive force of a Smee, which at first sight appears to favour the contact theory. If, however, quantitative measurements are made, it is shown that the electromotive force commences with a value higher than that of a Daniell, but rapidly sinks to, and remains perfectly constant at 0.732 D. No satisfactory explanation of this phenomenon can be furnished by the contact theory. A satisfactory explanation however is offered by the chemical theory, bearing in mind that oxygen from the air is readily soluble in acidulated water. If we had an ideal Smee, with absolutely no oxygen in solution, its value would be 0.732 D; if, on the other hand, all the hydrogen, instead of being deposited on the platinum plate, were oxidised to water by the dissolved oxygen, the value of the electromotive force would rise to 2.15 D: this never occurs in practice, but so long as any dissolved oxygen is present, the electromotive force will be higher than the "theoretical." Changing the negative plate to copper, carbon, &c., does not alter the electromotive force, provided the negative plate remains chemically unacted on.

The author made his measurements by a Branly's quadrant electrometer, the pairs of quadrants being kept at a constant difference of potential by a Zamboni's pile, one pole of the battery (Smee or Daniell) being connected with the biscuit of the electrometer, the other pole to earth, but so arranged that the cell could, at any moment, be readily short-circuited. The initial observed value of the Smee was 1.15 D, rapidly falling on closing to 0.731 D, at which it remained constant. The author objects to the compensation method, as oxygen may be so readily deposited on the platinum plate; however, by keeping the battery closed and merely connecting momen-

tarily to measure, he obtained the number 0.73 D. In using the ordinary form of Smee, a further falling off below 0.73 takes place after long closing, according as the acid is replaced by zinc sulphate; the author kept his plates in separate vessels connected by tubes containing acidulated water, thus completely preventing mixture.

The author concludes that the so-called galvanic polarisation does not exist in battery cells, every cell being unpolarisable; he thoroughly confirms the supposition of W. Thomson (*Phil. Mag.* [4], 2), arrived at from a consideration of the chemical reactions in the cell, that the nature of the negative plate is indifferent, so long as it remains chemically unchanged. F. L. T.

Efficiency of Secondary Piles. By E. REYNIER (*Compt. rend.*, 92, 1093—1096).—The effective value of a secondary pile is expressed by the ratio between the difference of potential of the two extremities of the resistance overcome, and the initial electromotive force of the source of electricity; it is independent of the resistances and the times of charge and discharge. The resistances, however, affect the times of charge and discharge, and must therefore be taken into consideration for practical purposes. The efficiency of a Faure pile depends to a great extent on its feeble internal resistance. Under favourable conditions of charge and discharge its yield is 80 per cent. C. H. B.

Thermal Electrolysis. By J. H. GLADSTONE and A. TRIBE (*Phil. Mag.* [5], 11, 508—510).—Some of the metals, either in the rolled or in the crystalline state, when immersed in their fused chlorides, become studded with crystals of the metal. The electrolysis which thus takes place is caused by a current, consequent on the unequal heating of the fused chloride; for according to the contact theory of voltaic action, there will be a difference of potential between the metal and the fused chloride in contact with it, and this difference of potential, varies with the temperature which, under the conditions of the experiment, could not be uniform.

That such is the case was proved with reference to silver and cuprous chloride, and in the case of the former one experiment showed a difference in the potential of possibly one-fiftieth of a volt.

The chlorides of the metals used (silver, copper, zinc, and iron), when fused, are electrolytes; from stannic chloride, which is not an electrolyte, no deposition of crystals was obtained on immersing tin in the unequally heated liquid.

These experiments on the conversion of heat into electric and chemical force form a good example for illustration at the lecture table. L. T. O'S.

Action of the Haloïd Acids on Salts containing the same Haloïd Elements. By BERTHELOT (*Ann. Chim. Phys.* [5], 23, 94—101).—Dry chlorides, bromides, and iodides of sodium, potassium, ammonium, and silver, absorb respectively 5—7 times their volume of gaseous hydrochloric, hydrobromic, or hydriodic acids. The absorp-

tion, which is accompanied by a distinct development of heat, is least marked in the case of the ammonium salts. The compounds formed are decomposed by mercury with liberation of hydrogen. They are probably analogous to the hydrochlorides previously described, but cannot exist in presence of water, since their heat of formation is less than that of the hydrate of the particular haloïd acid, and consequently the acid unites with the water in preference to combining with the salt.

C. H. B.

Reciprocal Displacement of the Haloïd Acids. By BERTHELOT (*Ann. Chim. Phys.* [5], 23, 102—110).—The action of the haloïd acids on haloïd salts is generally the reverse of that of the halogens themselves; hydriodic acid displaces hydrobromic acid, and the latter displaces hydrochloric acid. These facts are in accordance with thermochemical theories. For example, the formation of the system $\text{HCl} + \text{AgI}$ develops + 13.3 cals. more than the formation of $\text{HI} + \text{AgCl}$, and the formation of $\text{HCl} + \text{AgBr}$ develops + 7.0 cals. more than the formation of $\text{HBr} + \text{AgCl}$. Similar differences are observed with the salts of copper, mercury, lead, &c. In the case of the alkaline salts, however, the thermal differences are much more feeble, and are sometimes *nil*; the formation of $\text{HCl} + \text{NaBr}$, for example, develops sensibly the same amount of heat as the formation of $\text{HBr} + \text{NaCl}$. In these cases a slight difference in the specific heats, physical condition, and relative proportions of the reacting bodies, and the formation of secondary compounds, will determine the nature of the reaction. The formation of hydrochlorides of the chlorides, and hydrobromides of the bromides especially will exercise a considerable influence. When heated in a current of hydrochloric acid gas, dry sodium bromide is partially decomposed, sodium chloride being formed. This decomposition is in all probability due to the formation of a hydrobromide of the bromide, and if this compound were stable, the metal would be equally divided between the two halogens: for the reaction $2\text{HBr} + 2\text{NaCl} = \text{NaBr.HBr} + \text{HCl} + \text{NaCl}$ develops the same amount of heat as the reaction $2\text{HCl} + 2\text{NaBr} = \text{NaBr} + \text{HBr} + \text{HCl} + \text{NaCl}$. But the hydrobromide can only exist in presence of an excess of its constituents, and is dissociated, consequently the extent of the decomposition varies with the temperature, duration of the experiment, and other conditions. The decomposition of potassium and silver bromides by hydrochloric acid gas, is also, in all probability, due to the intermediate formation of a hydrobromide. This decomposition of the bromides by hydrochloric acid proceeds much less readily than the reverse reaction, the decomposition of the chlorides by hydrobromic acid.

The author finds that the haloïd salts volatilise to an appreciable extent at a dull red heat, especially in a current of gas, and that the haloïd acids act on glass at high temperatures, hydrochloric acid, for example, forming water and fixed and volatile chlorides which are partially decomposed by water.

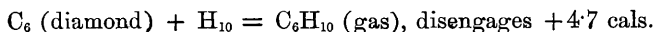
C. H. B.

Thermochemistry of Double Decomposition in Aqueous Solutions of Salts. By A. POTILITZIN (*Bull. Soc. Chim.* [2], 35,

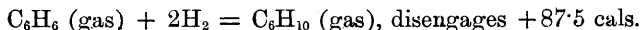
561—562).—A continuation of the author's researches (this vol., p. 6). The author has put forward the opinion that thermochemical phenomena observed in double decomposition, do not represent the total affinity—work in the predominant reaction, but only the algebraical sum of two inverse reactions. The calorimetric results are therefore proportional to the rapidity of the reactions in the first few seconds. If, then, one of the changes is effected by an absorption of heat, this is abstracted partly from the surrounding medium and partly from the reaction, which at the same time disengages heat. To confirm these views, the author has studied the reactions between the soluble and insoluble combinations of the halogens with hydrogens and the metals. It was shown by experiment that on the one hand the double decomposition between AgBr and HCl , LiCl , NaCl , and KCl is effected at ordinary temperatures by the borrowing of energy from the surrounding medium, and on the other hand that the action of NaBr and KBr on AgCl is never complete. In the first case the displacement reaches 1—2 per cent., in the second 91—95 per cent., in four days, the coefficient of displacement increasing with the mass. The author proposes to study the velocity and limit of the reactions.

V. H. V.

Heat of Formation of various Carbon Compounds. By BERTHELOT and OGIER (*Bull. Soc. Chim.* [2], 36, 66—69).—(1.) Heat of combustion of diallyl—

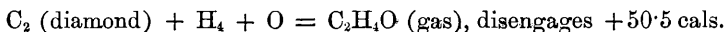


Conversion of dipropargyl into diallyl—



It is to be observed that this number surpasses the heat of hydrogenation of all hydrocarbons known.

(2.) Heat of combustion of aldehyde—



Heat of formation of acetic acid—



(3.) Dimethyl methylal—

Heat of combustion (as gas)	= +440.7 cal.
Specific heat	0.521 „
Heat of solution in 75 parts of water	3.2 „
Heat of vaporisation	6.83 „
Heat of formation $\text{C}_3 + \text{H}_8 + \text{O}_2 = \text{C}_3\text{H}_8\text{O}_2 \text{ (gas)}$..	6.83 „

(4.) Methyl formate—

Heat of combustion (gas)	+238.7 „
Specific heat	0.516 „
Heat of solution in 35 parts of water	1.13 „
Heat of vaporisation	6.91 „
Heat of formation $\text{C}_2 \text{ (diamond)} + \text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_4\text{O}_2$	87.3 „

Formic acid—

Heat of formation $C + H_2 + O_2 = CH_2O_2$	= +93.0 cal.
Heat of vaporisation	4.77 „
Specific heat	0.552 „

(5.) Ethyl formate—

Heat of combustion (gas)	+388.0 „
Specific heat	0.510 „
Heat of vaporisation	7.43 „
Heat of solution	+2.1 „
Heat of formation C_3 (diamond) + $H_6 + O_2 = C_3H_6O_2$	+101.0 „

(6.) Methylene chloride—

Heat of combustion	+106.8 „
Specific heat	0.288 „
Heat of formation C (diamond) + $H_2 + Cl_2 = CH_2$ (gas)	+31.2 „

(7.) Ethylidene chloride—

Heat of combustion	+267.1 „
Specific heat	0.315 „
Heat of vaporisation	6.63 „
Heat of formation C_2 (diamond) + $H_2 + Cl_2 = C_2H_2Cl_2$ (liquid ?)	40.5 „

(8.) Acetic chloride—

Specific heat	0.367 „
Heat of vaporisation	6.19 „
Heat of formation $C_2 + H_3 + Cl + O = C_2H_3ClO$ (gas)	67.9 „

(9.) Substitution phenomena—

Methyl series	$\left\{ \begin{array}{l} CH_4 + Cl_2 = CH_3Cl + HCl \text{ disengages} \\ CH_3Cl + Cl_2 = CH_2Cl + HCl \end{array} \right.$	+32.0 „
		„ +24.8 „
Ethyl series	$\left\{ \begin{array}{l} C_2H_6 + Cl_2 = C_2H_5Cl + HCl \\ C_2H_5Cl + Cl_2 = C_2H_4Cl_2 + HCl \end{array} \right.$	+54.8 „
		„ +17.4 „

The heat disengaged decreases with each replacement of the hydrogen-atom. V. H. V.

Heat of Combustion of Alcohols of the Allyl Series. By LONGUINE (*Bull. Soc. Chim.* [2], 35, 563—566).—The author has found for the heat of combustion of allyl-dimethyl carbinol 914,031 cal., and for allyl dipropyl carbinol 1,544,993 cal. These results, added to those formerly obtained by the author, show that for every CH_2 grouping added to allyl alcohol, the heat of combustion is increased by 157,478 cal., approximately equal to the number 157,000 obtained in other homologous series.

The heat of combustion of diallyl-methyl carbinol, $C_8H_{14}O$, was found to be 1,201,429 cal., which differs from that of the alcohol, $C_8H_{16}O$, by 28,611 cal., whilst the heat of combustion of the alcohol, $C_8H_{18}O$, differs from that of the alcohol, $C_8H_{14}O$, by 56,970 cal.; thus show-

ing that every H_2 added to the molecule increases the heat of combustion by about 28,482 cal.

The heat of combustion of normal caproic acid was found to be 830,209 cal., a number rather less than that disengaged by the combustion of 2 mols. of allyl alcohol, but approximately equal to that of 2 mols. of acetone. On comparing the heats of combustion of caproic acid and of allyl dimethyl carbinol, it is found that the introduction of 1 atom of oxygen diminishes the heat disengaged by about 83,822 cal.

V. H. V.

Vapour-density of the Halogens. By V. MEYER (*Ber.*, **14**, 1543—1545).—Experiments made at a yellow heat show that the molecules of the halogens dissociate. The values obtained for the densities of the gases at this temperature lie between X_1 and X_2 . The dissociation takes place most readily with iodine, and least easily with chlorine, *e.g.*, a temperature which causes a diminution in the density of iodine of 50 per cent. only lowers the density of chlorine 16 per cent. Arsenic and phosphorus at a yellow heat exhibit densities which lie between the values for As_4 or P_4 and As_2 or P_2 . The density of glucinum chloride could not be determined, since it loses chlorine even when it is volatilised in an atmosphere of nitrogen. Volatilised in an atmosphere of hydrochloric acid gas, ferrous chloride yields values between those for $FeCl_2$ and Fe_2Cl_4 .

W. C. W.

Absorption of Gases by Solids. By J. B. HANNAY (*Chem. News*, **44**, 3).—The author has repeatedly noticed the apparent disappearance of gases inclosed in vessels of various materials, when the disappearance could not be accounted for on the assumption of ordinary leakage. After a careful examination it was found that the solids absorbed or dissolved the gases, giving rise to a striking example of the fixation of a gas in a solid without chemical action. Out of 34 experiments made, only 4 contained any liquid or condensed gaseous matter after the furnacing, although in most cases a careful testing by hydraulic pressure showed no leakage. The solid matter at the very high pressure and temperature used is pervious to gases to a very remarkable extent. Glass at a temperature of about 200° absorbs large quantities of gas when the latter is under a pressure of 200 atmospheres; oxygen and carbonic anhydride were used. Other silicates, and also borates and phosphates, absorb gas. Metals absorb hydrogen and some of its compounds with carbon.

D. B.

The Passive State of Iron. By E. RAMANN (*Ber.*, **14**, 1430—1433).—The author points out that the explanation which Varenne (*Compt. rend.*, **79**, 783) gives of the passive state of iron, viz., that the metal is protected by a layer of nitrous acid, was proposed fifty years ago by Mousson (*Pogg. Ann.*, **39**, 330), and was shown to be utterly untenable by Schönbein and Beetz (*Pogg. Ann.*, **39**, 642; **67**, 286 and 365). Iron is rendered passive when it is heated in the air, when it forms the positive electrode of a galvanic couple, and also when it is immersed in any of the following liquids: nitric acid, solutions of the nitrates of ammonium, iron, silver, aluminium, nickel,

and cobalt. The passive state is due to a firm coating of the magnetic oxide on the surface of the metal, this oxide being sparingly soluble in strong nitric acid, but freely soluble in dilute. Finely divided iron, which has been immersed in any of the above liquids, and has been carefully dried in a current of an indifferent gas, may be shown to contain a considerable quantity of oxide, by the formation of water when ignited in a current of hydrogen.

When iron is dipped in nitric acid, a portion of the metal dissolves, forming ferric nitrate, which is reduced to ferrous nitrate by the excess of iron. A further reduction then takes place, the ferrous nitrate being converted into ammonia and magnetic oxide of iron: $4\text{Fe}(\text{NO}_3)_2 + 8\text{H}_2\text{O} + 11\text{Fe} = 4\text{NH}_4\text{NO}_3 + 5\text{Fe}_3\text{O}_4$. When ammonium nitrate acts on metallic iron, nitrosyl-ammonium, NH_4NO , is formed as an intermediate product.

The action of cobalt and nickel on their nitrates appears to be analogous to that of iron.

W. C. W.

Reaction without the Intervention of a Solvent. By LORIN (*Compt. rend.*, **92**, 1231—1234).—Further experiments confirm the results previously obtained (this Journal, **36**, 689). Formic acid is an acid of considerable chemical activity, and displaces, more or less, all acids. Its power of combination is intermediate between that of the organic acids and that of the most active inorganic acids. The energy of the action of acids on salts depends on their action on the bases of the salts. If an acid combines energetically with a certain base, its action on a salt of that base will develop a considerable amount of heat. As a rule, the action of a series of acids, for example, the fatty acids, on the same salt, develops less heat the higher the position of the acid in the series. Conversely the action of the same acid on salts of the fatty acids with the same base develops more heat the higher the position of the fatty acid. Formic acid, for example, develops more heat with acetates than with formates, with propionates than with acetates. The action of propionic acid on zinc oxide, and of butyric and valeric acids on baryta, does not conform to the general rules. The parallelism between the action of an acid on a base and its action on salts of that base, is not absolute. In some cases the reacting acid and the acid set free act upon one another, and thus the action of the former on the particular salt appears to be more energetic than it really is. In their mode of action, formic and lactic acids show a great similarity, but the latter acts on potassium dichromate with much greater energy than the former. The action of other acids on members of the series of fatty acids is less energetic the higher the position of the fatty acid in the series.

C. H. B.

So-called "Chemical Repulsion." By E. LECHER (*Wien. Akad. Ber.*, **82** [2], 159—163).—E. J. Mills (*Proc. Roy. Soc.*, **30**, No. 200) took two glass plates, in one of which there were two openings; he spread some solution of barium chloride on the lower, and placed the other, with the holes in it, on the first, thus forming a thin layer between the two of a solution of barium chloride. Into both the holes in the upper plate sulphuric acid was dropped; the reagent

spread out in circles from both centres, but the circles became oval, and finally ceased to extend towards each other, leaving a slight clear space between them, called by Mills a "line of no chemical action." As these two circles never mixed in his experiments, Mills concluded that there was a "chemical repulsion" between them, and he considered that this phenomenon indicated that chemical action can take place at a distance.

The author considers some point between the two rings when they are already somewhat near each other; the barium chloride molecules are moving equally in all directions, but when they come into contact with the advancing sulphuric acid they are prevented from returning, so that the space between the two advancing circles becomes void of barium chloride molecules, and the reaction consequently ceases to be further propagated. The author mixed a solution of barium chloride with one of potassium ferrocyanide, precipitated the barium by sulphuric acid, and still found that ferric chloride gave a blue reaction. When, however, the mixture of barium chloride and potassium ferrocyanide is placed between the plates, and a ring is produced by sulphuric acid, a subsequent addition of ferric chloride produces no action, showing that all the potassium ferrocyanide molecules have been mechanically removed.

By placing a concentrated solution of ferric chloride between the plates, and dropping potassium ferrocyanide into one hole, a blue girdle is produced, surrounded by a broad strip as clear as water, the solution of ferric chloride itself having a strong yellow colour between the plates. Two such circles approaching each other, an apparent repulsion naturally occurs, but this apparent repulsion also takes place on the reaction approaching the carefully cleaned edge of the glass plate, a fine "line of no chemical action" occurring.

The author, by laying a circular plate with a hole at its centre upon a somewhat larger one, and allowing ferric chloride from the outside to act upon the contained potassium ferrocyanide, succeeded in obtaining a clear circular space round the central opening surrounded by the blue girdle. Ferric chloride dropped into this clear space produces no reaction, but if instead potassium ferrocyanide be dropped into it the girdle becomes narrower, and finally leaves no trace whatever of "no chemical action."

In consequence of the above-mentioned experiments, the author cannot but conclude that the phenomena described by Mills do not require for their elucidation any new hypothesis of the nature of action at a distance.

F. L. T.

Inorganic Chemistry.

Densities of Liquid Oxygen, Hydrogen, and Nitrogen in Presence of Inert Liquids. By L. CAILLETET and P. HAUTEFEUILLE (*Compt. rend.*, **92**, 1086—1090).—The authors have determined the

densities of oxygen, hydrogen, and nitrogen in the liquid state by determining the densities of liquid mixtures of these gases with carbonic anhydride and nitrous oxide (compare this vol., p. 677), on the assumption that each constituent of the mixtures retains its own proper volume. Their results are given in the following table:—

Temp.	Pressure in atmos.	Density in the liquid mixture.		
		Oxygen.	Hydrogen.	Nitrogen.
0°	200	0.58	—	—
	275	0.65	0.025	0.37
	300	0.70	0.026	0.38
-23°	200	0.84	—	0.41
	250	—	—	0.42
	275	0.88	0.032	0.43
	300	0.89	0.033	0.44

The mixtures employed contained respectively 1 vol. oxygen and 7 vols. carbonic anhydride; 1 vol. hydrogen and 8 vols. carbonic anhydride; 1 vol. nitrogen and 11.36 vols. carbonic anhydride. The liquid mixtures are more compressible, and expand more rapidly than carbonic anhydride alone. The addition of even 0.4 per cent. by weight of hydrogen causes the carbonic anhydride to increase considerably in volume, and alters its expansibility and critical point, but does not give it the power of conducting electricity.

The coefficients of dilatation of liquid oxygen, hydrogen, and nitrogen between 0° and -23° are practically the same, and the three liquids are under comparable conditions. Their atomic volumes at -23° are: oxygen, 17; hydrogen, 30.3; nitrogen, 31.8. The atomic volume of nitrogen is almost double that of phosphorus, but if the atomic weight of the latter is taken as 62.8, a number corresponding with its specific gravity in the gaseous state, the two volumes are equal. The atomic volume of hydrogen is a little more than double the atomic volume of magnesium, with which it has been compared by Dumas. The temperature, -23°, is not sufficiently low for the atomic volume of oxygen to equal that of sulphur, 16. The values thus obtained for the atomic volumes of these three elements in the free state differ considerably from those deduced from the molecular volumes of their compounds.

C. H. B.

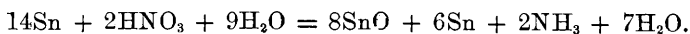
Proportion of Carbonic Anhydride in the Air. By A. MUNTZ and E. AUBIN (*Compt. rend.*, 92, 1229—1230).—Since December, 1880, the proportion of carbonic anhydride in the air, taken 6 meters from the ground, at the Conservatoire des Arts et Métiers, Paris, has varied between 2.88 and 4.22 in 10,000. When the air was still the proportion varied from 3.22—4.22 in 10,000. During breezy weather the amount was lower, varying from 2.89—3.1, practically the same as that present in country air. The highest proportions were found during heavy snow falls, or thick fogs.

Air taken 4 meters from the ground, at a station near the farm of the Institute of Agriculture, contained, during the day, from 2.70—

2.99 vols. of carbonic anhydride in 10,000, the mean being 2.85. During the night the mean was 3.00 vols. These results confirm those of Reiset (this Journal, **36**, 744, and **38**, 605). The proportion of carbonic anhydride in the normal air varies within narrow limits; the mean amount found in the neighbourhood of Paris is very little different from that found at Dieppe. The maximum variation observed by the authors is 3 in 100,000, a variation identical with that found by Reiset. It would appear that the carbonic anhydride diffuses with great rapidity, and should be uniformly diffused through the different layers of the atmosphere.

C. H. B.

Action of Nitric Acid on Metals. By E. J. MAUMENÉ (*Bull. Soc. Chim.* [2], **35**, 598—599).—It is well known that by the action of very dilute nitric acid on tin, stannous nitrate and ammonia are produced. By rapid rotation of a gyratory apparatus, and taking care that the nitric acid comes only gradually in contact with the tin, the author has realised the necessary conditions for the conversion of the tin into the protoxide, and of the nitric acid into ammonia, which may be expressed by the equation—



Other metals gave similar results, dependent upon the conditions of the reaction.

V. H. V.

Sulphuretted Hydrogen. By P. CASAMAJOR (*Chem. News*, **44**, 44). Skey, in 1873, published some interesting observations on the production of sulphuretted hydrogen when a voltaic couple is formed with zinc as the positive, and a metallic sulphide as the negative pole. The author has applied this to the production of sulphuretted hydrogen from iron sulphide, which refused to give it in presence of sulphuric acid diluted with ten times its volume of water.

Enough mercury is put in a bottle to cover the bottom entirely; on to this diluted sulphuric acid is poured, and some pieces of zinc are thrown in, which immediately sink into the mercury, forming a zinc amalgam with great excess of mercury. No action takes place between the zinc and the acid. If now a few pieces of iron sulphide are thrown into the bottle, a copious production of sulphuretted hydrogen will take place from the surface of the sulphide. The mercury only intervenes indirectly in the reaction, and does not require to be renewed. In place of iron sulphide, galena, iron pyrites, and copper pyrites have been tried. These all give sulphuretted hydrogen, but very slowly.

D. B.

Heat of Vaporisation of Sulphuric Anhydride. By BERTHELOT (*Bull. Soc. Chim.* [2], **35**, 545).—The heat of vaporisation of sulphuric anhydride was determined by comparing the heat disengaged by dissolving the gaseous and the solid anhydride in water.

The author found for SO_3 (gas) + H_2O + Aq = H_2SO_4 dilute = +49.2 cal., and for SO_3 (solid) + H_2O + Aq = H_2SO_4 dilute = +137.4 cal.: hence the heat of vaporisation of SO_3 (80 grams) = -11.8, a number approximately equal to the heat absorbed by the same volume of water = -12.3 cal.

V. H. V.

Hydrochlorides of Metallic Chlorides, and the Reduction of the Chlorides by Hydrogen. By BERTHELOT (*Ann. Chim. Phys.* [5], 23, 85—93). Many metallic chlorides form definite compounds with the haloid acids. The increased solubility of lead, silver, and cuprous chlorides in concentrated hydrochloric acid is probably due to such a combination. The heat of formation of these compounds from the gaseous haloid acid and liquid water is usually not much greater than the heat of solution of the acid in the water. When cadmium chloride is precipitated from its aqueous solution by concentrated hydrochloric acid, and a current of hydrochloric acid gas is passed into the liquid, the compound $\text{CdCl}_2 \cdot 2\text{HCl} + 7\text{H}_2\text{O}$ is obtained, in hard, brilliant, sometimes voluminous crystals, which rapidly decompose on exposure to air, losing hydrochloric acid. On the other hand, fused anhydrous cadmium chloride absorbs traces of hydrochloric acid gas, even at high temperatures. Hydrobromide of cadmium bromide was prepared in the same way, and evidence of the existence of a hydriodide of cadmium iodide was obtained, but this compound could not be isolated, owing to the ease with which it dissociates. The author was unable to isolate the hydrochloride of lead chloride, but by passing hydriodic acid gas into water containing lead iodide in suspension, and leaving the solution to cool, the compound $\text{PbI}_2 \cdot \text{HI} + 5\text{H}_2\text{O}$ was obtained in clear yellow crystals, which dissociate when exposed to air and light, hydriodic acid being given off, and a small quantity of iodine set free. When heated, the crystals decompose, leaving a residue of lead iodide. By dissolving silver iodide in hydriodic acid, and exposing the solution to the air, hydriodide of silver iodide, $3\text{AgI} \cdot \text{HI} + 7\text{H}_2\text{O}$, was obtained in transparent, crystalline lamellæ, which decompose when exposed to air and light. Another hydriodide, extremely soluble in hydriodic acid, also appears to exist. All these compounds are decomposed by water with absorption of heat, mainly due to the liquefaction of the solid water contained in the hydrate. Their heats of formation, as determined by means of this decomposition, are given in the following table:—

CdCl_2	+	2HCl	gas	+	$7\text{H}_2\text{O}$	liquid	develops	+	40.2	cals.
"	"	"	solid	"	"	"	"	+	30.0	"
PbI_2	+	HI	gas	+	$5\text{H}_2\text{O}$	liquid	"	+	23.3	"
"	"	"	solid	"	"	"	"	+	16.1	"
3AgI	+	HI	gas	+	$7\text{H}_2\text{O}$	liquid	"	+	21.6	"
"	"	"	solid	"	"	"	"	+	11.6	"

The total heat of formation is made up of the heat of formation of the hydrochloride and its heat of hydration, the latter in all probability being but small.

The decomposition of mercurous chloride by hydrochloric acid, with production of mercuric chloride and free mercury, is probably due to the intermediate formation of a hydrochloride; and the conversion of mercurous chloride into mercuric chloride by the action of alkaline chlorides is probably due to the intermediate formation of a double chloride. The formation of hydrochlorides probably plays an im-

portant part in the reduction of certain metallic chlorides by hydrogen.
C. H. B.

Hydrates of Calcium Chloride. By H. LESCŒUR (*Compt. rend.*, **92**, 1158—1161).—Determinations of the maximum tensions of mixtures of calcium chloride and water clearly indicate the existence of three distinct hydrates, $\text{CaCl}_2 + 6\text{H}_2\text{O}$, $\text{CaCl}_2 + 4\text{H}_2\text{O}$, and $\text{CaCl}_2 + 2\text{H}_2\text{O}$, and point to the probable existence of a monohydrate, $\text{CaCl}_2 + \text{H}_2\text{O}$. The authors conclude, with Wullner, that the hexahydrate can exist at 100° , but only in presence of an excess of water. If attempts are made to isolate it, it splits up into $\text{CaCl}_2 + 4\text{H}_2\text{O}$ and water. The tetrahydrate exists only at temperatures below 129° . Thomsen's thermo-chemical researches indicate the existence of the tetra- and hex-hydrates only.
C. H. B.

Action of Carbonic Anhydride on Barium and Strontium Oxides. By F. M. RAOULT (*Compt. rend.*, **92**, 1110).—Like quicklime (this vol., p. 348) barium and strontium oxides, when strongly heated, readily absorb carbonic anhydride, becoming incandescent. Barium oxide becomes more luminous than strontium oxide, and strontium oxide more luminous than calcium oxide. The temperatures are: with calcium oxide, 900° ; strontium oxide, $1,050^\circ$; and barium oxide, $1,200^\circ$. In no case can the normal carbonate be produced by direct synthesis.

Barium dioxide, when heated to redness, is decomposed by carbonic anhydride, with evolution of oxygen and development of much heat, which, however, is not sufficient to maintain the mass for any length of time at the temperature at which the decomposition takes place.

C. H. B.

Crystallisation of Alums. By A. LOIR (*Compt. rend.*, **92**, 1166—1169).—The author finds (1) that when a crystal with some of its angles or edges broken off is placed in a saturated solution of the same salt, the reconstruction of the fractured parts proceeds more rapidly than the growth of the crystal as a whole; (2) that different faces of a crystal have different powers of attraction for the solution in which they are placed. These facts are very evident when isomorphous salts of different colours are employed. When a crystal of ordinary alum, with some or all of its edges or solid angles broken off, is placed in a saturated solution of chrome-alum, the original regular form of the crystal is restored by the deposition of chrome-alum, and if the fractures have not been very deep, it is easy to see that the reconstruction of the mutilated edges and angles has been more rapid than the growth of the faces left intact. If two similar crystals, one unaltered, the other mutilated, are placed in the same solution, it is found after some time that the latter has increased in weight more rapidly than the former, and the difference is greater the deeper the fractures. A cube may be regarded as an octohedron with its solid angles much truncated, and it behaves in the same way as an octohedron with its angles broken off, so that when a cubic crystal of alum is placed in a solution giving octohedral crystals, it increases in weight more rapidly in proportion to the original weight than an octo-

hedron placed in the same solution. On the other hand, if a cube and an octohedron are placed in a solution giving cubic crystals, the latter grows more rapidly than the former. When a cubo-octohedral crystal of ordinary alum is placed in a solution of chrome-alum, the latter is deposited much more rapidly on the faces of the cube than on those of the octohedron. If the immersion is continued for a sufficient length of time, the whole surface of the crystal becomes covered with chrome-alum, which, however, is always much thicker on the faces of the cube. Similar results have been obtained with irregularly developed crystals.

C. H. B.

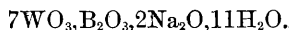
Decomposition of Water by Metallic Iron. By E. RAMANN (*Ber.*, 14, 1433—1434).—Finely divided metallic iron slowly decomposes boiling water. For example, 12 c.c. of hydrogen were obtained by boiling 10 grams of iron (prepared by reduction in hydrogen) in water for an hour.

Iron amalgam cannot be prepared by heating together dry sodium amalgam and finally powdered metallic iron, but if a small quantity of water is added to the mixture, a copious evolution of hydrogen takes place, and an amalgam of iron is formed.

By carefully squeezing the product to remove the excess of mercury, a crystalline amalgam is obtained which contains 15.75 per cent. of iron corresponding to the formula Hg_3Fe_2 . The amalgam slowly undergoes spontaneous decomposition. It rapidly decomposes when subjected to strong pressure.

W. C. W.

Sodium Tungstoborate. By D. KLEIN (*Bull. Soc. Chim.* [2], 35, 495—497).—A continuation of the author's former researches (this vol., p. 8). On evaporating sodium boroduodecitungstate to dryness with a large excess of hydrochloric acid, the tungstic acid separates out, and on taking up with water the sodium tungstoborate dissolves. The salt is very soluble in water, and crystallises out in regular octohedra; it has the constitution $9\text{WO}_3, \text{B}_2\text{O}_3, \text{Na}_2\text{O}, 3\text{H}_2\text{O}$. By treating in a similar manner a hydrochloric acid solution of sodium biborodecitungstate, clinorhombic crystals are obtained of composition—



These formulæ the author gives with all reserve.

V. H. V.

Cadmium Tungstoborate. By D. KLEIN (*Bull. Soc. Chim.* [2], 35, 492—495).—On adding a warm solution of barium chloride to a concentrated boiling solution of tetra-sodium duodecitungstate, the barium salt is precipitated. On suspending the precipitate in water acidulated with hydrochloric acid it dissolves, and, on evaporation, the bibarium tungstoborate separates out in magnificent octohedrons of the composition $9\text{WO}_3, \text{B}_2\text{O}_3 + 2\text{BaH}_2\text{O}_2 + 18\text{H}_2\text{O}$. On decomposing the barium salt with cadmium sulphate, the corresponding cadmium salt is obtained of the composition $9\text{WO}_3, \text{B}_2\text{O}_3 + 2\text{CdH}_2\text{O}_2 + 13\text{H}_2\text{O}$.

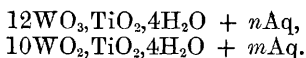
The author remarks on the similarity of crystalline form and sp. gr. of the corresponding salts of metatungstic and tungstoboric acids. He also proposes to use a nearly saturated solution of cadmium tungs-

toborate of sp. gr. 3.28, as a means for separating the mineral constituents of rocks of varying sp. gr., instead of a solution of potassium mercury iodide, which has been adopted for this purpose.

V. H. V.

The Titanotungstates. By D. KLEIN (*Bull. Soc. Chim.* [2], 36, 17—18).—This paper contains the researches of the late Raoul Lecarme on the titanotungstates. According to this chemist, the titanotungstates are separable into two classes, the titanoduodecitungstates analogous to the silicoduodecitungstates of Marignac, and the titanodecitungstates analogous to the silicodecitungstates.

These acids are tetrabasic; their formulæ are—



In order to obtain the acids, the insoluble mercurous salts are decomposed by hydrochloric acid, and the liberated acid evaporated in a vacuum. The author alludes to the variety of combinations of tungstic acid, and their analogy to homologous series of organic compounds.

V. H. V.

Silico-Molybdates. By F. PARMENTIER (*Compt. rend.*, 92, 1234—1235).—Ammonium silico-molybdate is obtained in small yellow octohedrons, by mixing nitric acid solutions of ammonium molybdate and an alkaline silicate. It may be purified by solution in water, from which it is precipitated on addition of an ammonium salt. The silico-molybdates of potassium and sodium may be obtained in a similar manner. Thallium silico-molybdate is formed when either of the preceding compounds is decomposed by a thallium salt. It is a dense crystalline yellow powder, but the form of the crystals cannot be determined. Analysis of these salts leads to the formula $2\text{RO} \cdot \text{SiO}_2 \cdot 13\text{MoO}_3 + n\text{H}_4\text{O}$. The ratio of base to acid is 1 : 7, a ratio frequently observed in the compounds of molybdic acid. The author has obtained white, perfectly crystallised silico-molybdates, containing less silica than the preceding compounds, and less soluble.

C. H. B.

Solubility of Silver Chloride in Hydrochloric Acid. By F. RUYSEN and E. VARENNE (*Bull. Soc. Chim.* [2], 36, 5—11).—The solubility of silver chloride in hydrochloric acid has been studied by Stas, Pierre, and more recently by Ditte (this vol., p. 786).

The method of procedure adopted by the author was as follows: a standard solution of silver nitrate was added to the requisite quantity of a standard solution of hydrochloric acid, and then the excess of the same solution required to dissolve the known weight of precipitate obtained was determined. The authors found that 1 part of silver chloride required 244 parts of hydrochloric acid for solution. Although the addition of water decreases the solubility coefficient, yet the decrease is not directly proportional to the quantity of water so added. Thus for eight times the quantity of water added, the solubility coefficient is only doubled. The presence of foreign metals assists the solution to a slight degree. It was ascertained that the presence of mercurous chloride retards to an extraordinary degree the solution of

silver chloride, one part of which in presence of even a small quantity of mercurous chloride requiring 3,158,152 parts of hydrochloric acid.

V. H. V.

Amalgams. By V. MERZ and W. WEITH (*Ber.*, **14**, 1438—1447).—The authors have exposed amalgams of gold, silver, copper, lead, tin, bismuth, zinc, and cadmium, to the temperature of boiling sulphur, boiling mercury, and boiling diphenylamine for several hours, and find that the mercury is completely or almost completely expelled. Amalgams of potassium or sodium lose their mercury slowly. The melting points of these amalgams are interesting.

Sodium.	Melting point.	Potassium.	Melting point.
3.0 per cent.	152—160°	2.7 per cent.	75°
4.7 "	305—315	3.7 "	160—170°
9.3 "	276—299	4.7 "	175—184
14.0 "	170—190	6.5 "	198—206
29.2 "	175—180	9.8 "	240—245
37.9 "	152—159	18.2 "	175—185
— "	—	29.8 "	147—152

W. C. W.

Solubility of Mercurous Chloride in Hydrochloric Acid. By F. RUYSSSEN and E. VARENNE (*Compt. rend.*, **92**, 1161—1163).—The solubility of mercurous chloride in hydrochloric acid, unlike that of silver chloride, depends on the time during which it has remained in contact with the acid. The following table gives the amount of freshly precipitated mercurous chloride dissolved by different quantities of the concentrated acid.

c.c. of Acid.	Containing HCl.	Hg ₂ Cl ₂ dissolved.	Ratio between weight of Hg ₂ Cl ₂ dissolved, and weight of acid.
262	115.0931 grams	0.0136 gram	1 : 8,462
712	312.1764 "	0.0272 "	1 : 11,845
1,146	502.4637 "	0.0408 "	1 : 12,316
1,250	548.0625 "	0.0544 "	1 : 10,075
6,000	2630.7000 "	0.1088 "	1 : 24,179

The coefficient of solubility decreases as the quantity of mercurous chloride present increases. When the mercurous chloride is left in contact with the acid for several days, it slowly dissolves until a point is reached, perhaps due to the conversion of the mercurous into mercuric chloride, at which solution proceeds rapidly. For example, 50 c.c. of acid which had dissolved with difficulty 0.0816 gram mercurous chloride in seven days, dissolved as much as 0.6526 gram during the last hour of the seventh day. The smaller the quantity of acid present, the sooner is this period of accelerated solubility reached. From the following table, which gives the maximum quantities of mercurous chloride dissolved by different volumes of hydrochloric acid of 7 per cent., it will be seen that the final coefficient of solubility diminishes as the quantity of acid increases.

Acid used.	Hg ₂ Cl ₂ dissolved.
25 c.c.	0·984 gram.
50 „	1·990 „
75 „	0·947 „
100 „	2·437 „
375 „	5·259 „

Mercurous chloride is more soluble in hydrochloric acid in presence of silver chloride than when alone. The following table gives the quantity dissolved in both cases, the silver and mercurous chlorides being present in equivalent proportions :—

HCl.	Hg ₂ Cl ₂ dissolved.	
	Alone.	In presence of AgCl.
25	0·984	1·048
50	1·990	3·846
75	0·947	3·007
100	2·437	3·965
375	5·259	10·436

When hydrogen sulphide is passed into a hydrochloric acid solution of silver chloride and mercurous chloride, a precipitate is formed, the colour of which varies from bright yellow to orange-yellow, according to the relative proportions in which the two chlorides are present.

C. H. B.

Action of Flame on Platinum. By A. REMONT (*Bull. Soc. Chim.* [2], 35, 486).—It is generally supposed that the carbonaceous deposit formed on platinum when heated in a reducing flame contains so small a proportion of platinum that it may be neglected in most determinations. But the author obtained in a particular case by the calcination of 0·022 gram of such a deposit, 0·01 gram of the metal. He considers this disintegration of the metallic platinum to be due to the combined action of the carbon and the high temperature; but in the case of burning gas, it is caused not by carbon in suspension, but rather by one or more of the gaseous constituents of the flame.

V. H. V.

Organic Chemistry.

Monobromethylene. By M. KUTSCHEROFF (*Ber.*, **14**, 1532—1539).
—Attempts to prepare an aldehyde by the action of water, water and lead oxide, moist silver acetate, or silver oxalate on monobromethylene were unsuccessful, the monobromethylene decomposing into acetylene and hydrobromic acid. On oxidation with chromic acid or potassium permanganate, monobromethylene yields formic, carbonic, and oxalic acids. The formation of aldehyde, when monobromethylene is treated with sulphuric acid or mercuric acetate, is due to a secondary reaction.

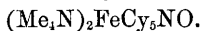
Acetylene is formed in the first instance, and this is converted into aldehyde by contact with water and mercuric bromide at the ordinary temperature, and also by the action of sulphuric acid.

W. C. W.

Direct Addition of Water to the Hydrocarbons of the Acetylene Series. By M. KUTSCHEROFF (*Ber.*, **14**, 1540—1542).—Acetylene is converted into aldehyde if it is left in contact with mercuric bromide and water at 100° in a sealed flask. Under similar conditions, allylene is converted into acetone, and valerylene into a ketone of the composition $C_5H_{10}O$.

W. C. W.

Organic Nitroprussides. By O. BERNHEIMER (*Wien. Akad. Ber.* [2], **80**, 328—330).—Tetramethylammonium nitroprusside is formed by precipitating sodium nitroprusside with silver nitrate, and acting on tetramethylammonium iodide with the silver nitroprusside. On concentrating the bright red filtered solution on the water-bath, it deposits fine ruby-coloured prismatic crystals often an inch long. No measurements could be made on account of the rapid efflorescence on exposure to the air. The air-dried salt contained $\frac{1}{2}H_2O$. The composition of the dried salt agrees with the formula



It is very readily soluble in alcohol and in water, not at all in ether. With the sulphides of the alkalis, the aqueous solution gives an intense purple-red colour, rapidly turning to blue, characteristic of the nitroprussides. Potassium hydroxide produces an orange colour. On heating the salt, complete decomposition occurs, with evolution of combustible gases.

Tetrethylammonium nitroprusside, $(Et_4N)_2FeCy_5NO$, is prepared in a precisely similar manner, and resembles the methyl compound very closely. It effloresces quite as readily, and the air-dried salt retains 1 mol. H_2O .

F. L. T.

Influence of Isomerism on the Etherification of Alcohols and Acids. By N. MENSCHUTKIN (*Ann. Chim. Phys.* [5], **23**, 14—81—Compare this vol., 36). The results given in the first part of this paper concerning the etherification of glycols and polyhydric alcohols have already been published (this vol., 144 and 146). As in the case of the monhydric alcohols, the primary glycols have the highest initial rate and limit of etherification, and the tertiary have the lowest, whilst the secondary and intermediate glycols occupy intermediate positions. The limit of etherification of the primary glycols is lower than that of the corresponding primary monhydric alcohols, and the same holds good for the secondary and tertiary glycols and alcohols. It would follow therefore that the decrease in value of the primary and secondary OH groups will be greater the higher the total number of such groups contained in the alcohol. This is probably the principal cause of the diminution in the limit of etherification for glycerol, erythrol, and mannitol. The decrease in the limit of etherification, with increase in the number of OH groups in an alcohol, leads to the supposition that polyhydric alcohols may exist, which will not yield

ethers by the direct action of acid, and the ethers of which, when formed, will be very readily decomposed by water. When an increasing number of molecules of acetic acid act on 1 mol. of glycerol, the rate of action is not uniform, but decreases as the number of molecules of the acid increases. This is not due to a difference in the functions of the OH groups, for a similar result is obtained with ethylene glycol, in which both the OH groups are primary.

Influence of Isomerism, &c., on the Etherification of Acids.—The same method of experiment was adopted as in the case of the alcohols, isobutyl alcohol and, in some cases, ethyl alcohol being employed. The purity of the acids was controlled by titration with standard baryta solution, rosolic acid being used as an indicator. With the primary acids, the exact point of neutralisation could be readily ascertained, but with the tertiary acids, the salts of which are easily decomposed by water, the determination of the end point of the reaction was much more difficult, owing to the persistence of the intermediate shades of colour.

Saturated Monobasic Acids.—The results obtained are given in the following table:—

Etherification of Isobutyl Alcohol at 155°.

	Initial velocity.		Limit.
	Absolute.	Relative.	
<i>Primary Acids—</i>			
Formic acid	61.69	96.04	64.23
Acetic acid	44.36	65.38	67.38
Propionic acid	41.18	59.94	68.70
Normal butyric acid	33.25	47.82	69.52
Normal caproic acid	33.08	47.38	69.81
Normal caprylic acid	30.86	43.26	70.87
<i>Secondary Acids—</i>			
Isobutyric acid	29.03	41.76	69.51
Methylethylacetic acid	21.50	29.16	73.73
<i>Tertiary Acids—</i>			
Trimethylacetic acid	8.28	11.39	72.65
Dimethylethylacetic acid	3.45	4.55	74.15

Etherification of Ethyl Alcohol at 155°.

	Initial velocity.		Limit.
	Absolute.	Relative.	
<i>Primary Acids</i> —			
Acetic acid	46.95	70.52	66.57
Normal butyric acid	36.00	52.34	68.77
Normal caproic acid	34.62	48.16	69.80
<i>Tertiary Acid</i> —			
Dimethylethylacetic acid ..	5.43	7.35	73.88

The initial rate of etherification, both absolute and relative, is

greatest for the primary, less for the secondary, and still less for the tertiary acids. The differences are so great that the initial rate of etherification may be employed as a means of determining the structure of an acid. For example, the absolute initial velocity for normal caproic acid is 33·08; that for the tertiary acid is only 3·45. With the primary acids, the rate of etherification rapidly diminishes, and the limit is soon reached; with the secondary acids, the diminution is more gradual, whilst in the case of tertiary acids, the progress of etherification is extremely slow, and it is necessary to heat the mixture of acid and alcohol for from 500 to 600 hours before the limit is reached; in fact, the limit for tertiary acids containing 7 and 10 carbon-atoms could not be determined. For all the acids, the initial rate decreases with an increase in molecular weight. In the case of the first three members of the primary series, the diminution is considerable, but the higher members show only slight differences, *i.e.*, above a certain molecular weight, the initial rate tends to become constant. The following numbers show that the difference between the etherification powers of two acids is the same, whether measured by their action on isobutyl or on ethyl alcohol:—

	Initial velocity.	
	Absolute.	Relative.
Acetic acid and isobutyl alcohol.....	44·36	65·38
Butyric acid „ „ „	33·25	47·82
Differences.....	11·11	17·54
Acetic acid and ethyl alcohol.....	46·95	70·52
Butyric acid „ „ „	36·00	52·34
Differences.....	10·95	18·18
Acetic acid and isobutyl alcohol.....	44·36	65·38
Tertiary caproic acid and isobutyl alcohol	3·45	4·65
Differences.....	40·91	60·73
Acetic acid and ethyl alcohol.....	46·95	70·52
Tertiary caproic acid and ethyl alcohol	5·43	7·35
Differences.....	41·52	63·17

From this it would follow that if the etherification rate of any alcohol with one acid is known, its rate with other acids of the same series can be calculated from the numbers given.

It would appear that, below a certain molecular weight, the constitution of an acid does not affect its power of etherification, butyric and isobutyric acids, for example, giving practically the same limits. On the other hand, the limit for tertiary caproic acid is higher than that of the normal acid, and it may be stated as a general rule that the secondary and tertiary acids give higher limits of etherification than the primary acids. The limit of etherification for acids of

analogous constitution increases with an increase in molecular weight. In the acetic series, the difference between the two successive acids diminishes as the series is ascended, and the limit tends to become constant.

The author made experiments with heptonic acid (m. p. 20—25°; b. p. 202—203°), and decoic acid (b. p. 250—253), obtained by M. Parloff by the oxidation of diamylene, with a view to determine their constitution. The initial rate of heptylic acid was 0.42, that of decoic acid 0.49; in neither case could the limit be determined. Both acids therefore belong, in all probability, to the tertiary series.

Non-saturated Monobasic Acids.—The following results were obtained:—

Primary Acids.

Series.	Acid.	Initial velocity.		Limit.
		Absolute.	Relative.	
$C_nH_{2n-2}O_2$	Hydrosorbic acid	43.00	60.70	70.83
"	" "	42.99	62.05	69.28*
$C_nH_{2n-3}O_2$	Phenylacetic acid	48.82	66.08	73.87
	Phenylpropionic acid ..	40.26	55.90	72.02

Secondary Acids.

$C_nH_{2n-2}O_2$	Crotonic acid	12.12	16.80	72.12
"	" "	11.64	16.57	70.23*
$C_nH_{2n-10}O_2$	Cinnamic acid	11.55	15.48	74.61

Tertiary Acids.

$C_nH_{2n-2}O_2$	Ethylcrotonic acid	2.97	4.27	69.26
$C_nH_{2n-4}O_2$	Sorbic "	7.96	10.65	74.72
$C_nH_{2n-6}O_2$	Benzoic "	8.62	11.87	72.56
"	Paratoluic "	6.64	8.69	76.52
"	Cuminic "	6.24	8.24	75.91

The etherification of the non-saturated monobasic acids is strictly analogous to that of the saturated acids. The initial rates are somewhat higher for the primary and tertiary non-saturated acids than for the saturated acids containing the same number of carbon atoms, and the differences are greater the less the degree of saturation of the non-saturated acids, *i.e.*, the more nearly an acid is saturated the lower is its rate of etherification. For the secondary acids, however, the reverse is apparently the case. The differences between primary and corresponding tertiary acids in the non-saturated series are more marked than similar differences in the saturated series. The etherification rates of hydrosorbic acid indicate that it is a primary acid. Its formula may, therefore, be either $CH_2:CPr.CO_2H$, or, as Fittig has proposed —



The initial rate of sorbic acid indicates that it is a tertiary acid, and it may have the constitution $PrC:C.CO_2H$. This point requires further investigation. As in the case of the saturated acids, the progress of

* With ethyl alcohol.

etherification is apparently slower with secondary and tertiary than with primary acids. Comparing the initial rates of the two series we have the following numbers :—

Saturated Acids.

Primary acids	30·86—44·36
Secondary „	21·05—29·03
Tertiary „	3·45— 8·28

Non-saturated Acids.

Primary acids	40·26—48·82
Secondary „	11·55—12·12
Tertiary „	2·97— 8·62

As in the saturated series, the constitution of an acid has but little effect on its limit of etherification, but the tertiary acids have a somewhat higher limit than the primary secondary acids. The non-saturated acids have a higher limit than the saturated acids containing the same number of carbon-atoms.

At 155° isocrotonic acid is converted into the secondary acid, and metacrylic acid is rapidly transformed into a solid polymeride; tetrolic acid splits up into allylene and carbonic anhydride. The etherification rates of these acids could not therefore be determined.

C. H. B.

Ethylene Chlorhydrin. By BERTHELOT (*Compt. rend.*, **93**, 185—190).—The readiness with which ethylene oxide combines directly with acids is easily explained on thermochemical principles. The reaction, $\text{C}_2\text{H}_4\text{O}$ (gas) + HCl (gas) = $\text{C}_2\text{H}_5\text{ClO}$ (liquid), disengages + 36 cals., a number which is comparable with the heat of formation of ammonium chloride, $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$ (solid), disengages 42·5 cals. These thermochemical phenomena bear out Wurtz's comparison of ethylene oxide to a base, which is further supported by the facts that ethylene oxide and hydrochloric acid combine even in very dilute solutions with sensible evolution of heat. This combination explains a reaction observed by Wurtz between ethylene oxide and the metallic chlorides, if it be granted that a small quantity of the chloride is decomposed by water present into the corresponding hydroxide and hydrochloric acid, which latter combines in its turn with the ethylene oxide. At the same time the comparison of ethylene oxide to a base is not complete, for this body will not combine with acetic acid in dilute solutions.

The heat of formation of ethylene chlorhydrin from glycol and hydrochloric acid is deduced by the author to be $\text{C}_2\text{H}_6\text{O}_2$ (liquid) + HCl (gas) = $\text{C}_2\text{H}_5\text{ClO}$ (liquid) + HO_2 (liquid) = + 17·1 cals., whilst from ethylene and hypochlorous acid it is $\text{C}_2\text{H}_4 + \text{HClO}$ (dilute) = $\text{C}_2\text{H}_5\text{ClO}_2$ (dilute) = + 66·9 cals.

V. H. V.

Relation of various Sugars to Fehling's Solution. By F. SOXHLET and others (*Bied. Centr.*, 1881, 268—272).—Soxhlet purifies dextrose by crystallisation from methyl alcohol, obtaining it in snow-white crusts; the compound, $\text{C}_6\text{H}_{12}\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$, he was unable to

produce. 1 mol. of purified milk-sugar he found reduced from 7.43 to 7.85 mols. of copper, lactose from 4.7 to 4.9, and maltose 6.09.

J. K. C.

Modification of Starch. By F. MUSCULUS (*Bied. Centr.*, 1881, 355).—Starch may be crystalline or colloid; when colloid it is soluble in water, is coloured blue by iodine, does not diffuse, and is easily attacked by ferments and acids; is readily converted by hot water into an insoluble condition, which is not attacked by acids and ferments, and is coloured red or yellow by iodine. After treatment with strong acids or soda it is reconverted into the first form. Crystalline starch is soluble in water up to 60°, diffuses and ferments; the separate crystals are not coloured by iodine, but the solution is coloured red, and becomes blue on evaporation.

E. W. P.

Lævulan: a new Species of Gum occurring in Beetroot Molasses. By E. O. v. LIPPMANN (*Ber.*, 14, 1509—1512).—The name *lævulan* is given by the author to a new species of gum which was found in the form of a gelatinous precipitate, on the walls and bottom of a reservoir, in which the refuse liquors from Steffen's process for desugarising molasses had remained for a considerable time during very cold weather. The precipitate is insoluble in lime-water, alcohol, water, and in a solution of sugar. It was purified by the method which Scheibler employed (*Zeitschrift für Rübenzucker Industrie*, 1874, 309) for the purification of dextran.

Pure lævulan, $C_6H_{10}O_5$, is a white amorphous body, which melts at 250° with complete decomposition. The anhydrous compound dissolves in hot water, and on cooling the solution solidifies to a colourless jelly. After continued boiling it becomes soluble in cold water. The precipitate, which is thrown down on the addition of alcohol to a neutral solution of lævulan in lime-water, is soluble both in cold and in hot water. Lævulan is strongly lævogyrate, its specific rotatory power being -221° . It is converted into lævulose by the action of dilute sulphuric acid at 120°, and on oxidation it yields mucic acid.

W. C. W.

Chloropropaldehyde. By E. GRIMAUX and P. ADAM (*Bull. Soc. Chim.* [2], 36, 22—24).—By the direct combination of acrolein with hydrochloric acid, Geuther and Cartmell obtained a crystalline substance, which was shown subsequently by Krestownikoff (*Abstr.*, 1880, 234) to be α -chloropropaldehyde, $CH_2Cl.CH_2.CHO$. By exposing acrolein saturated with hydrochloric acid to a freezing mixture, the authors obtained the para-chloropropaldehyde in the form of large transparent needles (m. p. 33.5°); it distils without alteration at 170—175° under a pressure of 12—15 mm. It is a very stable compound, and has no cupric oxide reducing power.

By distilling parachloropropaldehyde with potassic hydroxide, the authors prepared metacrolein, which crystallises in large transparent plates (m. p. 45°); its vapour-density, 5.8, corresponded with the formula C_3H_4O . Metacrolein in chloroform solution readily takes up bromine, and is converted into dibromopropaldehyde, $C_3H_4Br_2O$.

V. H. V.

Action of Acetone on Furfuraldehyde and on Benzaldehyde in presence of Alkalis. By J. G. SCHMIDT (*Ber.*, **14**, 1459—1461).

—The compound, which the author obtained by warming a mixture of acetone and furfuraldehyde with a solution of sodium hydroxide (*Ber.*, **14**, 575; this volume, 573), crystallises in long colourless needles. The substance melts at 37.5° , and distils with partial decomposition at 229° . Its formation is due to the following reaction:— $3C_5H_4O_2 + 2C_6H_6O = C_{21}H_{20}O_6 + 2H_2O$. It is decomposed by boiling with dilute acids, and on oxidation with silver oxide yields a fluorescent solution. A similar act of condensation takes place when 10 parts of sodium hydroxide solution (10 per cent.) are added to 900 parts of water, containing 10 parts of benzaldehyde and 20 parts of acetone. The mixture is gently warmed and on cooling deposits pale yellow crystalline plates or needles (m. p. 110°). This compound has the composition $C_{41}H_{34}O_3$. It is soluble in chloroform, ether, strong sulphuric acid, and hot alcohol.

W. C. W.

Brominated Propionic and Acrylic Acids. By J. MAUTHNER and W. SUIDA (*Wien. Akad. Ber.*, **83** [2], 273—296).—*Tribromopropionic Acid*.—In order to prepare one of the isomeric tribromopropionic acids, the monobromacrylic acid of Phillippi and Tollens was treated with the necessary quantity of bromine. On crystallising the crude product of the reaction from light petroleum, tribromopropionic acid separates out in the form of long colourless prisms (m. p. 95°) of the monoclinic system, which bear some resemblance to the crystalline form of dibromopropionic acid. The *barium* salt is obtained by neutralising an alcoholic solution of the acid with barium carbonate; it contains either 4 or 5 H_2O . The author considers it probable that the acid here described is identical with that of Linnemann and Penl (*Ber.*, 1875, 1097), and possibly with that of Michael and Norton. When an aqueous solution of barium tribromopropionate is heated to 130° , it is decomposed into barium bromide, carbonic anhydride, and unsymmetrical dibromethylene.

Dibromacrylic Acid.—On treating tribromopropionic acid with the necessary quantity of alcoholic potash, hydrobromic acid is easily removed, and the dibromacrylic acid can be separated out by petroleum. This acid forms a warty crystalline mass (m. p. 85°), soluble in most menstrua; it is undoubtedly identical with the acid obtained by Jackson and Hill (*Abstr.*, 1879, 224). The *lead* salt forms crystalline leaflets, the *silver* salt long silky glistening needles.

The authors found that their acid, like that of Jackson and Hill, when heated with barium hydroxide, gives considerable quantities of malonic acid. On heating the barium salt at 180° for some hours with water, it is decomposed with formation of unsymmetrical dibromethylene.

Tetrabromopropionic Acid.—This acid is best obtained from dibromacrylic acid by heating the latter to 100° with the necessary quantity of bromine. On crystallising from light petroleum, this acid separates in colourless tables (m. p. 125°), melting to an oil under water, and soluble in most menstrua. It was found impossible to isolate its salts; an aqueous solution of the acid neutralised with barium carbonate is

decomposed into barium bromide, carbonic anhydride, and tribromethylene.

Tribromacrylic Acid.—On treating tetrabromopropionic acid with the necessary quantity of alcoholic potash at a temperature not exceeding 60° , hydrobromic acid is removed with formation of tribromacrylic acid. This acid separates out from petroleum in prisms (m. p. 117°), soluble in most menstrua; the *barium* and *calcium* salts form silky glistening needles. An acid identical in melting point but not in crystalline form was previously obtained by the authors by the removal of hydrobromic acid from tribromopropionic acid by excess of alkali, and subsequent bromination of the bromopropiolic acid formed. By heating with water at 120° barium tribromacrylate is decomposed into barium carbonate, carbonic anhydride, and tribromethylene.

Experiments with a view of obtaining pentabromopropionic acid by the bromination of tribromacrylic acid failed; this the authors consider to be due to the fact that hexbrom- and hexchlor-ethane readily lose a molecule of the halogen.

The authors found that the β_2 -dibromopropionic acid when heated with excess of alkali is decomposed with formation of acetylene. With regard to the constitution of the acids above described, the authors start from the dibromacrylic acid of Jackson and Hill (*vide supra*), which yields malonic acid, and has the probable constitution—



It is decomposed by alkalis, with formation of unsymmetrical dibromethylene, $\text{CBr}_2 : \text{CH}_2$.

The tribromopropionic acid is probably the α_2 - β -acid,



and the monobromacrylic from which it is formed is the α -acid, $\text{CHBr} : \text{CH}.\text{COOH}$. The tetrabromopropionic acid obtained by the oxidation of α -dibromacrylic acid has the formula $\text{CBr}_3.\text{CHBr}.\text{COOH}$, whilst for the tribromacrylic acid there is only one possible formula, $\text{CBr}_2 : \text{CH}.\text{COOH}$. The authors' researches show that the haloïd derivatives of propionic acid are more readily decomposed, with formation of substituted ethylenes, than their derived acrylic acids. The authors further point out that the successive introduction of bromine-atoms into propionic acid increases the melting point by about 30° , whilst the introduction of bromine in the α -position of acrylic acid increases the melting point by about 15° , but in the β -position by about 32° .

V. H. V.

Ethyl Mono- and Di-chlorothiactates: Action of Phosphorus Pentasulphide on Chlorinated Acetic Acids. By P. J. MEYER (*Ber.*, **14**, 1507—1509).—*Ethyl dichlorothiactate*, $\text{CHCl}_2.\text{COSEt}$, formed by the action of phosphorus pentasulphide on ethyl dichloracetate at 160 — 180° , is an oily liquid boiling at 118° , and heavier than water. It is decomposed by aqueous ammonia and by water. With alcoholic ammonia, it forms a compound, crystallising in prisms. *Ethyl monochlorothiactate*, $\text{CH}_2\text{Cl}.\text{COSEt}$, obtained by the action of phosphorus pentasulphide on ethyl monochloracetate at

120—140°, boils at 167°, and resembles the preceding compound in other respects. Satisfactory results could not be obtained by acting on the free chloracetic acids with phosphorus pentasulphide.

W. C. W.

Separation of Suberic and Azelaic Acids. By F. GANTTER and C. HELL (*Ber.*, 14, 1545—1552).—The authors have examined the properties of several mixtures of suberic and azelaic acids, with special reference to their crystalline form and melting points. The results are contained in the accompanying table. They have also examined the different methods employed for the separation of these acids, and have arrived at the following conclusions:—

1. The separation can be effected by repeated recrystallisation from water, but this involves a considerable loss of material.

2. By treatment with cold ether, suberic acid can be obtained in a state of purity, but pure azelaic acid cannot be obtained in this way. 100 parts of ether at 15° dissolve 0·809 part of suberic acid and 2·68 parts of azelaic acid.

3. Fractional precipitation with calcium or manganese chloride yields pure azelaic acid, but not pure suberic acid.

4. By the fractional crystallisation of the magnesium salts both acids can be obtained in the pure state.

Composition.				Appearance of the fused mixture on cooling.	
Azelaic. Suberic. Molecules.		Azelaic. Suberic. Percentage.			Melting point.
				Degrees.	
10·0 + 0		100 + 0		106	Large four-sided plates ; pearly lustre.
9·5	0·5	95	5	104	Smaller plates.
9·0	1·0	90	10	103·5	The plates are rounded off ; opaque.
8·5	1·5	86	14	98·5	Large round masses, resembling porcelain in appearance.
8·0	2·0	81	19	98·0	Large round masses, surface perforated with cavities.
7·5	2·5	76	24	96·0	Ditto ditto
7·0	3·0	72	28	98—100	Smaller aggregations, less broken by cavities.
6·5	3·5	66	34	99—101	The resemblance to porcelain increases.
6·0	4·0	62	38	106—109	Ditto ditto
5·5	4·5	57	43	108—109	Ditto ditto
5·0	5·0	51	49	115	The surface penetrated by glistening needles.
4·0	6·0	42	58	123	The needles increase in number.
3·0	7·0	31	69	124—128	Surface no longer resembles porcelain, but is composed of slender crystals.
2·0	8·0	21	79	125—130	Larger needles.
1·0	9·0	10	90	135—136	} Long needles, in radiating groups ; vitreous lustre.
0·0	10·0	0	100	140	

The acids are, however, best separated by a combination of methods 2 and 4. The crude mixture of acids is recrystallised from hot water, fused, powdered, and frequently digested with 10 times its weight of ether. The ethereal solution contains a mixture of the two acids. The residue consists chiefly of suberic acid. The extract is evaporated to dryness, the residue dissolved in hot water, neutralised with magnesium carbonate, and the solution concentrated. The crystals which are deposited are pressed to remove the mother-liquor, and recrystallised from hot water. On the addition of hydrochloric acid to the magnesium salt, pure azelaic acid is obtained. The mother-liquor is rich in suberic acid, which may be precipitated by hydrochloric acid, and purified by treatment with ether. W. C. W.

Rotatory Power of Malic Acid and its Salts. By G. H. SCHNEIDER (*Annalen*, 207, 257—287).—In order to prepare pure malic acid, the author converts the commercial product into ammonium hydrogen malate, which separates out from the aqueous solution on addition of alcohol. The precipitated crystals are filtered off, washed repeatedly with ether, and finally crystallised from water. It is thus obtained in rhombic brachypinacoidal plates, from 10—20 mm. diameter.

The majority of the determinations of the angles of rotation were made with a Wild's polaristrobometer, fitted with an apparatus for keeping the temperature constant at 20°. The sodium flame was employed as a source of light. Some of the readings were made with Laurent's apparatus. Exact estimations of the sp. gr. of the liquids at 20° were made.

Specific Rotatory Power of Malic Acid, $C_4H_6O_5$.—The pure acid is best obtained by converting ammonium hydrogen malate into the lead salt, and then decomposing it with sulphuretted hydrogen. The solution is then evaporated, and the residue heated in a current of air at 100° until it ceases to lose weight. The last operation requires several weeks.

The author finds that when a dilute laevorotatory solution of malic acid is gradually concentrated, the specific rotatory power diminishes, and when the percentage of acid in solution reaches about 34 it disappears, and finally on further concentration the solution exhibits a dextrorotatory power.

As the relationship between the percentages of water and the specific rotatory power of the solutions can be represented by a straight line, the rotatory power of solutions of various strengths can be calculated by the formula—

$$[\alpha] = A + Bq.$$

The author shows that the anhydrous acid has a dextrorotatory power of 5.89°. A solution containing 34.24 per cent. of acid is inactive. A solution with an infinite amount of water (*i.e.*, $q = 100$) has a laevorotatory power of -3.068° .

Potassium hydrogen malate, $KC_4H_5O_5$, is prepared by heating a solution of ammonium hydrogen malate with the calculated amount of potassium hydroxide solution, and then adding the requisite amount of malic acid. Air is blown through the liquid during the heating, in

order to facilitate the removal of ammonia. The author finds that the formula $[\alpha] = A + Bq$ can also be employed here. It gives for the anhydrous salt a specific rotatory power -0.63° . An infinitely diluted solution has a rotatory power -6.19° . *Potassium Malate*, $K_2C_4H_4O_5$.—This salt is prepared in a manner similar to the preceding one. In this case, the change of rotatory power being represented by a curve, the formula $[\alpha] = A + Bq + Cq^2$ is employed. The anhydrous salt has a rotatory power of $+3.02^\circ$, an infinitely diluted solution -7.31° . A solution containing 79.54 per cent. of the salt is optically inactive.

Sodium Hydrogen Malate, $NaC_4H_5O_5$.—The specific rotatory power of the anhydrous salt is $+9.37^\circ$. A solution containing 59.75 per cent. of the salt is inactive. When $q = 100$, the solution has a rotatory power of -7.02° . *Sodium Malate*, $Na_2C_4H_4O_5$.—The rotatory power of the anhydrous salt is $+15.2^\circ$, of the extremely dilute solution -9.84° . A solution containing 47.43 per cent. of the salt is optically inactive.

Lithium Hydrogen Malate, $LiC_4H_5O_5$.—The anhydrous salt has a power of $+8.57^\circ$, an infinitely diluted solution -8.48° . An inactive solution contains 71.865 per cent. of the salt. *Lithium Malate*, $Li_2C_4H_4O_5$.—The rotatory power of the anhydrous salt is $+26.72^\circ$, of the infinitely diluted solution -12.71° . A solution containing 50.48 per cent. of the salt is inactive.

Ammonium Hydrogen Malate, $NH_4C_4H_5O_5$.—The anhydrous salt has a rotatory power of -3.95° , the extremely dilute solution -6.83° . *Ammonium Malate*, $(NH_4)_2C_4H_4O_5$.—This salt decomposes very readily in the air, giving off ammonia. The rotatory power of the anhydrous salt is -3.31° , the infinitely diluted solution -8.93° .

Barium Malate, $BaC_4H_4O_5$.—This salt is prepared by boiling baryta water with a solution of ammonium hydrogen malate until ammonia ceases to be evolved. The gummy mass thus obtained is then decomposed with an excess of dilute sulphuric acid, neutralised with baryta-water, filtered, and after concentration allowed to stand. The salt crystallises out in thin transparent plates. The rotatory power of the anhydrous salt cannot be calculated with any degree of certainty; the author states, however, that it is evidently extraordinarily great.

Influence of Sulphuric Acid on the Specific Rotatory Power of Malic Acid.—The author finds that the direction of rotation begins to change even in very dilute solutions.

Influence of Acetic Acid.—The influence of acetic acid is similar to that exercised by sulphuric acid, but more feeble. A mixture of the two acids in the proportion of 20 mols. of acetic acid to 1 of malic acid has the same rotatory power as a mixture of 2 mols. of sulphuric acid to 1 of malic acid.

The author shows that malic acid and its salts do not yield results which support the law of multiple rotatory proportion. J. I. W.

New Isomeride of Gluconic Acid. By M. HÖNIG (*Wien. Akad. Ber.* [2], 80, 1047—1054).—There are already three acids

known of the formula $C_6H_{12}O_7$, derived from the carbohydrates, viz., mannitic, gluconic, and dextronic acids.

Mannitic acid, according to Gorup-Besanez (*Annalen*, **118**, 259), exchanges two atoms of hydrogen for metal on being acted on by carbonates, and generally yields readily soluble and uncrystallisable salts, gluconic and dextronic acids merely exchanging one atom of hydrogen for metal, and yielding readily crystallisable salts of the alkaline earths, but not of the alkalis. These two acids differ (Habermann, *Annalen*, **162**, 297) only somewhat in the solubility of their salts and in the molecular rotation of the free acids.

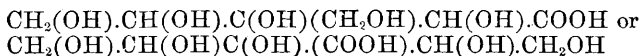
The author, by acting on the driest possible gluconic acid with two to three times its weight of nitric acid of sp. gr. 1.3 at the ordinary temperature, and then neutralising with aqueous ammonia and evaporating, obtained a crystalline ammonium salt of an organic acid of the same composition as gluconic acid, but differing from it in that the salts of the alkalis are crystalline and the salts of the alkaline earths are amorphous. The author proposes to call it *paragluconic acid*. The ammonium salt, $C_6H_{11}(NH_4)O_7$, remains unchanged at 120°, becoming brown at 120—130°, and giving off a little ammonia, but on dissolving the mass in water and purifying by animal charcoal, unchanged ammonium paragluconate crystallises out on evaporating.

Free paragluconic acid, obtained by decomposing the lead salt with sulphuretted hydrogen, and evaporating over sulphuric acid in a vacuum, is an almost colourless syrup with a strongly acid taste, showing no trace of crystallisation even on standing for months. Like gluconic acid, it is insoluble in strong alcohol, and its aqueous solution is not precipitated by metallic salts.

Hlasiwetz and Habermann, by the action of chlorine, &c., on cane-sugar, obtained the same products as from grape-sugar, and amongst them gluconic acid, whilst Grieshammer (*Ber.*, **12**, 2100) found an acid isomeric with gluconic acid, yielding crystalline salts both of the alkaline earths and of the alkalis.

There are now five isomeric acids of the formula $C_6H_{12}O_7$ known, which by no means exhaust the number of possible isomeric acids of this formula.

The author examines the possible structural formulæ, and taking into consideration that paragluconic acid by oxidation yields saccharic acid, and eventually tartaric and oxalic acids (*Wien. Akad. Ber.*, **78**, 2 Abth., 1878), considers either



to be the most probable formula.

F. L. T.

New Acid of the $C_nH_{2n-4}O_6$ Series. By A. BAUER and M. GRÖGER (*Wien. Akad. Ber.* [2 Abth.], **82**, 164—166).—The authors prepare suberic acid by oxidation of oleic acid, purify it by Arppe's method, and convert it into monochlorosuberic acid by acting on the fused acid with an amount of chlorine insufficient to convert all the acid, thus avoiding the production of higher chlorinated derivatives. The monochlorosuberic acid was separated by treating the product

with ether, in which it is very soluble, whilst the sparingly soluble suberic acid remains.

When monochlorosuberic acid is digested with potassium cyanide with a reversed condenser for six hours, and then for ten hours more with potassium hydroxide, a powerful evolution of ammonia takes place, and after neutralisation with dilute sulphuric acid and extraction with ether, a brown crystalline mass is obtained. This is first treated with water to remove some sparingly soluble portion, probably unaltered suberic acid, then treated with blood-charcoal, converted into the neutral ammonium salt, and then into the lead salt. By decomposing this with sulphuretted hydrogen, an acid is obtained in small shining crystals, having the composition $C_6H_{11}(COOH)_3$. The normal silver salt, $C_9H_{11}Ag_3O_6$, is obtained as a white bulky precipitate on adding silver nitrate to a solution of the ammonium salt.

F. L. T.

A New Series of Volatile Organic Bases. By F. P. TREADWELL (*Ber.*, **14**, 1461—1471).—The author proposes to assign the name of *ketines* to the class of bases obtained by the reduction of the nitroso-derivatives of the ketones.

Diethylketine, $C_{10}H_{16}N_2$, is prepared by the action of tin and hydrochloric acid on nitrosoethyl-acetone, prepared by the process described by Züblin and V. Meyer. The tin is precipitated from the solution by sulphuretted hydrogen, and the filtrate concentrated by evaporation and mixed with an excess of solid soda. The oil which separates is removed, and the liquid is extracted with ether. The oily liquid and the ethereal solution are dried over calcium chloride and purified by distillation. The pure base is an oily liquid (b. p. 216°), which unites with water to form a white hydrate crystallising in needles (m. p. 42.5°). When the hydrate is placed in a desiccator over calcium chloride, it parts with its water and is converted into the anhydrous liquid base. Diethylketine hydrochloride forms large colourless crystals, and the platinochloride, $C_{10}H_{16}N_2 \cdot 2HCl \cdot PtCl_4$, crystallises in large glistening prisms of a rose colour. On the addition of bromine-water to a solution of diethylketine in glacial acetic acid, an addition-product, $C_{10}H_{16}N_2Br_2$, is obtained as a yellow precipitate. This compound is very unstable, and is decomposed into diethylketine and bromine by crystallisation from alcohol.

Dimethylketine, $C_8H_{12}N_2$, prepared by Gutknecht from nitrosomethyl acetone, but not obtained by him in a state of purity, forms small hard vitreous prisms (m. p. 87°). It combines with water to form a hydrate crystallising in silky needles. Dimethylketine is precipitated from its solution in an acid on the addition of an alkali.

Ketine and dipropylketine have been obtained from nitroso-acetone and nitrosomethyl acetone respectively.

W. C. W.

Ethylazaurolic Acid (Nitroso-Azoethane). By V. MEYER and E. J. CONSTAM (*Ber.*, **14**, 1455—1458).—Ethylnitrolic acid is decomposed by sodium amalgam into nitrous and acetic acids and ammonia. An intermediate product of reduction, viz., ethylazaurolic acid, is also formed (*Annalen*, **175**, 111), and can be most easily isolated by the following process:—40 grams of 5 per cent. sodium amalgam are

gradually added to 2 grams of ethylnitrolic acid suspended in 10 c.c. of water. The liquid must be well cooled in a freezing mixture. The temperature should be kept about 0° , but the liquid must not be allowed to freeze.

On acidifying the orange-coloured solution with dilute sulphuric acid, yellow needle-shaped crystals are precipitated, which are washed with a small quantity of cold water and quickly dried. When the experiment is successful, 0.18 gram of the substance can be obtained from 1 gram of ethylnitrolic acid. The pure acid crystallises in glistening prisms, which resemble potassium dichromate in colour. The crystals melt at 142° with detonation. They are soluble in hot alcohol and in alkalis, insoluble in chloroform, benzene, and light petroleum. Neutral solutions of the acid give yellow precipitates with zinc and lead salts, and a brown precipitate with silver nitrate. If a small quantity of the acid is dissolved in ammonia, a yellow solution is obtained, which on exposure to the air in a watch-glass deposits crystals of the free acid. The acid is decomposed by sodium amalgam, and also by boiling hydrochloric or sulphuric acids. Its constitution may probably be represented by the formula $\text{NO} \cdot \text{C}_2\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{NO}$. Propylazaurolic acid has been obtained by the reduction of propylnitrolic acid.

W. C. W.

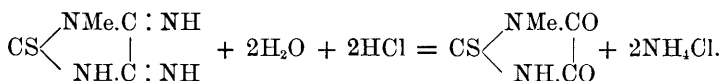
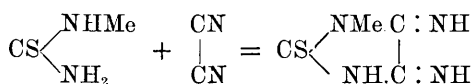
Synthesis of Biguanide. By R. HERTH (*Wien. Akad. Ber.*, **80**, [2], 1078—1088).—The action of an ammoniacal solution of cupric hydroxide on thiocarbamide gives rise to dicyandiamide, and as a secondary product a very small quantity of carmine-coloured needles. These needles were found to contain copper and sulphuric acid, the latter being derived from the small quantity of cupric sulphate retained by the ammoniacal cupric solution. By substituting cupric sulphate for the hydroxide, and heating in sealed tubes at 105 — 110° , a better yield is obtained, but the best method is to heat dicyandiamide with ammoniacal cupric sulphate at 105 — 110° for 12 hours. The crystals of sulphate of cupro-biguanide, $(\text{C}_2\text{N}_5\text{H}_6)_2\text{Cu} \cdot \text{SO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$, being insoluble in water, are easily washed. On dissolving it in the least possible excess of dilute sulphuric acid and leaving it for some time, eventually in a vacuum over sulphuric acid, well-formed clear rhombohedrons crystallise out, of the composition $\text{C}_2\text{N}_5\text{H}_7 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$. By heating dicyandiamide with ammoniacal cupric hydroxide for 8 to 10 hours, cupro-biguanide, $(\text{C}_2\text{N}_5\text{H}_6)_2\text{Cu} + 2\text{H}_2\text{O}$, is formed, and separates on cooling in large flat prisms.

From this body, the different biguanide salts may be obtained by the action of the corresponding acid, and removal of the copper by sulphuretted hydrogen. The author claims to have shown that—1. That by the action of an ammoniacal solution of cupric oxide on dicyandiamide, biguanide is produced. 2. That this method is satisfactory, both as regards yield and absence of secondary reactions.

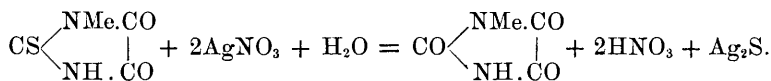
F. L. T.

Synthesis of Methylparabanic and Methylthioparabanic Acids, and of Thiocholesthophane. By R. ANDREASCH (*Ber.*, **14**, 1447—1453).—Direct combination takes place when cyanogen gas is passed into an alcoholic solution of methylthiocarbamide. Strong

hydrochloric acid is added to the crude product, and the mixture is evaporated to dryness on a water-bath. The aqueous solution of the residue is shaken up with ether, and on evaporating the ethereal extract, methylthioparabanic acid is obtained in thin yellow crystalline plates. The formation of the acid may be represented by the following equations:—



The acid is soluble in alcohol, ether, and water. It melts at about 105° . On the addition of silver nitrate to the aqueous solution of the acid, a yellow precipitate is formed which rapidly turns black; the filtrate contains methylparabanic acid (m. p. 149°).



Dimethylthioparabanic acid or Thiocholestrophane, $\text{CS} \begin{array}{l} \text{NMe.CO} \\ | \\ \text{NMe.CO} \end{array}$ is

formed from cyanogen and dimethylthiocarbamide by a process analogous to that for preparing methylthioparabanic acid.

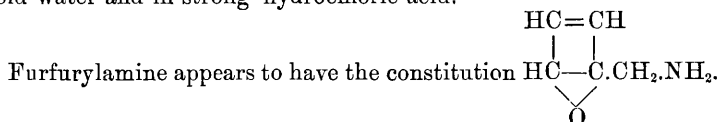
This acid crystallises in six-sided plates (m. p. 112.5°), resembling potassium chromate in colour. The crystals are soluble in water, alcohol, and ether. The acid is decomposed by alkalis into oxalic acid and dimethylcarbamide; when boiled with water containing barium carbonate in suspension, it splits up into sulphuretted hydrogen, carbonic anhydride, and dimethylloxamide. Dimethylthioparabanic acid is desulphurised by the action of nitrate of silver, cholestrophane (m. p. 105°) being formed. Mono- and di-methylparabanic acids are not precipitated by lead acetate, unless one or two drops of ammonia are added to the mixture: the precipitate consists of basic *lead oxalate*. All parabanic acids exhibit the following reaction: they do not yield a precipitate with a cold solution of ammonium chloride to which ammonia has been added, but on warming the mixture calcium oxalate is precipitated.

W. C. W.

Furfurylamine. By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, 14, 1475—1477).—Furfurylamine is best prepared by charging a series of small flasks each with two grams of furfuronitril, an excess of dilute sulphuric acid (1 in 20), and the requisite amount of zinc. The flasks are loosely corked and left at rest for two or three weeks. An excess of sodium hydroxide is then added to their contents, and the mixture is distilled in a current of steam. The distillate is neutralised

with hydrochloric acid and evaporated to dryness, and the residue is dissolved in a small quantity of water. Sticks of potassium hydroxide are added to this solution until the base begins to separate as an oil, the mixture is then shaken up with ether, and the oil which remains on evaporating the extract is purified by distillation. Furfurylamine is a strongly refractive oily liquid (b. p. 146°), miscible with water in all proportions. It is decomposed by strong hydrochloric acid. The hydrochloride prepared by carefully neutralising the base with hydrochloric acid, and evaporating in a vacuum, crystallises in colourless needles or prisms which are very soluble in water.

On the addition of platinum chloride to a colourless solution of the base in an excess of dilute hydrochloric acid, an orange-coloured precipitate is produced $(C_5H_7NO.HCl)_2PtCl_4$, which is sparingly soluble in cold water and in strong hydrochloric acid.



W. C. W.

Butylation of Aniline. By A. STUDER (*Ber.*, **14**, 1472—1475).—*Amidobutylbenzene hydrochloride*, $C_6H_4(NH_2)C_4H_9.HCl$, is prepared by heating 10 grams of dry aniline hydrochloride with 8 grams of isobutyl alcohol in sealed tubes at 230° for six hours. On recrystallisation from water containing hydrochloric acid, the salt is obtained in white prismatic tables. On the addition of platinum chloride to the concentrated aqueous solution of the hydrochloride, a red oil is deposited, which rapidly solidifies to a mass resembling shellac in appearance.

Amidobutylbenzene is a colourless oil (b. p. 230° , sp. gr. 0.937 at 25°). It enters into an active reaction with acetic chloride, forming the compound $C_6H_4(C_4H_9).NHAc$, which crystallises in white plates (m. p. 170°) soluble in alcohol and water.

When a mixture of 10 grams of aniline hydrochloride and 13 grams of isobutyl alcohol is heated at 240 — 250° for six hours, only a small quantity of amidobutylbenzene hydrochloride is formed, but a sparingly soluble salt or mixture of salts is obtained. The base liberated from the sparingly soluble hydrochloride is probably $C_6H_4(C_4H_9).NH.C_4H_9$. It forms an oily nitroso-compound, and an acetyl derivative which melts at 73° and boils above 300° .

Butylphenol, $C_6H_4(C_4H_9).OH$, obtained by acting on amidobutylbenzene with sodium nitrite and boiling the product with water, crystallises in long needles. It melts at 99° and boils at 231° . By the action of nitric acid on the acetic acid solution of butylphenol, the dinitro-derivative is produced. It crystallises in long needles (m. p. 93°) of a beautiful yellow colour, and plays the part of a powerful acid.

W. C. W.

Production of Hydrogen Peroxide by Hydrogenised Palladium.—Ozobenzene. By A. R. LEEDS (*Pharm. J. Trans.* [3], **11**, 1068—1070).—On exposing benzene to sunlight, in contact with oxygen, platinum black and a little water, the liquid in a short time

assumes a yellow colour, and after some days becomes dark yellow and intensely acid.

In repeating the experiments of Houzeau and Renard on the action of ozone on benzene, the author failed to obtain the white amorphous explosive solid (ozobenzene) isolated by them, but besides formic and acetic acids, he has obtained oxalic acid and large quantities of carbonic anhydride; not a trace of phenol was detected.

Since nascent oxygen oxidises water to hydrogen peroxide, whereas ozone does not, it appeared probable that a similar difference would be met with in their action on benzene. On exposing benzene in contact with water and nascent oxygen to direct sunlight, both phenol and oxalic acid were formed, and the liquid remained colourless; but in diffused light at 50—70° the liquid assumed a dark brown colour, oxalic acid was formed, but no phenol. The phosphorus used in these experiments to give nascent oxygen dissolves in the benzene at the ordinary temperature; at a higher temperature, although the flask is filled with dense white fumes, no ignition takes place, the benzene vapour apparently preventing it. After the oxalic acid has been separated from the solution as calcium oxalate, a yellow pasty mass is obtained from the filtrate, which cannot be made to crystallise, and has not been further examined.

On repeating Hoppe-Seyler's experiments (this Journal, **38**, 3) on the action of hydrogenised palladium on benzene, the author confirms his results, large quantities of phenol being formed, but no oxalic acid; this is produced by the action of hydrogen peroxide on the benzene, $C_6H_6 + HO.OH = C_6H_5OH + OH_2$, as is shown by the fact that hydrogenised palladium in contact with water and air, yields hydrogen peroxide, and that by treating benzene with a 1·2 per cent. solution of hydrogen peroxide, first at the ordinary temperature for two days, and then for several days at the temperature of the water-bath, phenol and oxalic acid are formed.

L. T. O'S.

Crystallisable Constituents of Corallin. By C. ZULKOWSKY (*Wien. Akad. Ber.*, **80** [2], 157—186).—Since the publication of the author's work on "Corallin" (*Chem. Soc. J.*, 1878, **33**, 832), other papers have appeared by E. and O. Fischer (*Ber.*, 1878, 1426), by Dale and Schorlemmer, and by A. Bayer (*Ber.*, 1879, 642), and he complains that these do not sufficiently recognise his share in the solution of the corallin question.

In preparing corallin the author considers that it is not necessary to heat the mixture of phenol and sulphuric acid to complete the formation of sulphophenol, as described in his earlier work. The amount of sulphuric acid may also be reduced from two-thirds to half part: he obtained good results by mixing 1 part phenol with half part sulphuric acid (66° B.), then adding 0·6—0·7 part dehydrated oxalic acid, and heating to 120—130° until the contents of the flask on cooling formed a viscid mass, and the evolution of gas had decidedly diminished. About 24 hours are required to complete the process, and the yield varies from 60—70 per cent.

The separation of the corallin-phthalin was performed as described in the former paper (*Annalen*, **194**, 109), the residue from this heated

at 120° to free it from sulphurous acid, and then crystallised from alcohol; the same products, however, did not always occur in the same order as formerly.

Oxidised aurin (violet needles, $C_{19}H_{16}O_6$). This body, formerly termed "violet needles" by the author, crystallises out from a solution of purified corallin on leaving it at rest. The whole was purified by recrystallisation from 50 per cent. alcohol. It was found that it would not do to boil the alcohol, the body being then reduced to leucaurin, as much as 70 per cent. being destroyed in the course of six hours' boiling.

By the action of sulphurous acid or of sodium hydrogen sulphite on oxidised aurin, a compound of aurin with sulphurous acid is formed of the composition $2(C_{19}H_{14}O_3) + H_2SO_3$. By acting on oxidised aurin with acetic anhydride, and throwing the solution into excess of water, *diacetyl-aurin*, $C_{23}H_{20}O_6$, is obtained, showing that the oxidised aurin is in the first place reduced by the acetic anhydride.

The author considers that oxidised aurin probably contains one molecule of water, although it will not part with this water without undergoing further decomposition. By oxidising aurin with sodium manganate, the author obtained oxidised aurin. On boiling oxidised aurin or the artificially prepared product in fine powder, in glacial acetic acid, it dissolves to a dark yellow-red fluid, which on cooling solidifies to a mass of vermilion-coloured crystals, having the composition of the diacetate, $C_{19}H_{13}O_5(HO\dot{A}c)_2 + H_2O$. On standing in a vacuum over lime and sulphuric acid at the ordinary temperature, half of this acetic acid is given off, forming the monacetate.

Leucaurin ($C_{19}H_{16}O_3$).—Gräbe and Caro have prepared and described (*Annalen*, **179**, 190) a triacetyl derivative from the homologous compound $C_{20}H_{18}O_3$ (the rosolic acid from rosaniline). The acetyl derivative of leucaurin was obtained in a similar manner by boiling it in fine powder for a quarter of an hour in acetic anhydride. It dissolves rapidly, and triacetyl-leucaurin, $C_{19}H_{13}(O\dot{A}c)_3$, is precipitated as a white powder on pouring the solution into water; it can be recrystallised from alcohol. By oxidising leucaurin with manganates, an amorphous mass was obtained of the composition of auringuinone, $C_{19}H_{14}O_4$, but it could not be crystallised.

Aurin ($C_{19}H_{14}O_3$).—The compound of aurin with sulphurous acid is easily prepared by dissolving aurin in potassium hydroxide, adding sodium hydrogen sulphite to decolorisation, and then concentrated hydrochloric acid so long as a precipitate continues to form.

Methylaurin ($C_{20}H_{16}O_3$).—The author has separated this body from corallin in small brick-red crystals with a green metallic lustre. It might be thought that this body owed its formation to the presence of cresol in the phenol used, but on replacing a portion of the phenol by cresol, no crystalline body whatever is produced, but a tarry mass with no metallic lustre. The author considers that it is not a derivative of tolyldiphenylmethane, but rather of triphenylethane, and that it stands to corallin-phthalein in the relation represented by the formulæ—

Methylaurin..... $(\text{C}_6\text{H}_4.\text{OH})_2\text{C} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}_2 \end{smallmatrix} > \text{O}.$

Corallin-phthalein $(\text{C}_6\text{H}_4.\text{OH})_2\text{C} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} > \text{O}.$

To a hot saturated solution of methylaurin in 60 per cent. alcohol, about 10 per cent. by volume of concentrated hydrochloric acid is added, and the whole left to crystallise; large well-formed occasionally radiating columnar crystals with bright red colour and sky-blue fluorescence then separate out, of the composition $\text{C}_{23}\text{H}_{24}\text{ClO}_4$. By employing the same methods with methylaurin as with aurin, compounds are obtained with sulphurous acid, but of varying composition. By oxidation with sodium manganate a body, $\text{C}_{19}\text{H}_{11}\text{O}_3$, is obtained. The attempts to make an acetyl derivative did not lead to any definite result.

Leucomethylaurin ($\text{C}_{20}\text{H}_{18}\text{O}_3$).—On dissolving the leuco-product of methylaurin in acetic anhydride, and leaving it in a vacuum over lime and sulphuric acid, crystals, and subsequently resinous masses, are deposited. The crystals have the appearance and composition of leucaurin. The leuco-product boiled for a quarter of an hour with acetic anhydride and then poured into water, gives a resinous precipitate, becoming crystalline on moistening with alcohol; on recrystallisation its composition is $\text{C}_{22}\text{H}_{21}\text{O}_6$ or $\text{C}_{22}\text{H}_{20}\text{O}_6$, therefore not the expected compound $\text{C}_{20}\text{H}_{15}(\text{O}\ddot{\text{A}}\text{c})_3$, but it might be regarded as the monacetyl derivative of some body, either $\text{C}_{20}\text{H}_{19}\text{O}_5$ or $\text{C}_{20}\text{H}_{18}\text{O}_5$.

F. L. T.

Tannin of Oak-bark. By J. LÖWE (*Anal. Zeits.*, **20**, 208—223).—Oak-bark tannin is not, as is usually believed, a glucoside, furnishing glucose and oak-bark red on treatment with acid, but is simply transformed by dehydration into the latter substance, with formation of very small amounts of intermediary products.

For the preparation of the oak-bark tannin in a pure state, the bark is extracted with 90 per cent. alcohol, the alcohol removed from the solution by distillation, and the residue treated with water in which it partly dissolves, yielding a dark-brown solution, and leaving a reddish-brown insoluble substance. The solution, when saturated with sodium chloride, deposits tannic anhydride; whilst the solution, on treatment with ether (in which the oak-bark tannin is practically insoluble) yields to the latter some gallic and ellagic acids. After the removal of the ether, the solution is shaken with acetic ether, in which the tannin dissolves, and is obtained in the form of a reddish-brown brittle mass. With ferric salts its solution gives a blue-black, with tartar-emetic, gelatin, albumen, or alkaloïds, yellowish-white precipitates.

Heated with dilute acids under pressure, the tannin readily yields oak-red.

The relation between the various products obtained is seen from the following formulæ:—

Two hydrates of tannic acid, $\text{C}_{28}\text{H}_{24}\text{O}_{12}, 3\text{H}_2\text{O}.$
 $\text{C}_{28}\text{H}_{24}\text{O}_{12}, 2\text{H}_2\text{O}.$

The lead salt, $\text{C}_{28}\text{H}_{18}\text{Pb}_3\text{O}_{12}, 5\text{H}_2\text{O}.$

Tannic anhydride, $C_{28}H_{24}O_{12}$.

Its lead salt, $C_{28}H_{22}PbO_{12} \cdot 3H_2O$.

Oak-red, $C_{28}H_{22}O_{11}$.

O. H.

Derivatives of Metachloronitrobenzene- and Orthochlorobenzene-sulphonic Acid. By R. ALLERT (*Ber.*, **14**, 1434—1438). — *Metachloronitrobenzenemonosulphonic acid* is formed when metachloronitrobenzene is heated with an excess of fuming sulphuric acid at 100° for five days. The barium, lead, and potassium salts of this acid crystallise in white needle-shaped crystals; the barium salt is but sparingly soluble in water. The free acid, prepared by the action of sulphuretted hydrogen on the lead salt, forms a yellow resinous mass. *Metachloronitrobenzenesulphonic chloride*, obtained by the action of phosphorus pentachloride on the potassium salt, is a yellow oil. On reduction with tin and hydrochloric acid, it yields metachloramidophenyl mercaptan, which crystallises in flesh-coloured needles. The crystals give off hydrochloric acid at 100° . The free base,



melts at 140° . No organic bases could be produced by the action of organic acids or acid chlorides on this compound.

Metachloronitrobenzenedisulphonic acid, $C_6H_2Cl(NO_2)(SO_3H)_2$, is prepared by adding successive small portions of metachloronitrobenzene to boiling Nordhausen sulphuric acid. The mixture must be repeatedly shaken to moderate the violence of the reaction. The crude product is diluted with water, neutralised with lead carbonate, and the acid liberated from the lead salt by sulphuretted hydrogen. The free acid is a black uncrystallisable substance. The lead and potassium salts crystallise in plates. The barium salt is quite insoluble in water.

Metachloronitrobenzenedisulphonic chloride is a brown resinous substance, which yields *metachloramidophenylldimercaptan hydrochloride* on reduction with tin and hydrochloric acid. The salt forms flesh-coloured crystals, which decompose slowly at 100° . The base,



contains the SH groups in the meta- and para-position with regard to the amido-group, and in the ortho- and meta-position to the chlorine atom.

Orthochlorobenzenesulphonic acid, which Limpricht (*Ber.*, **10**, 320, this Journal, 1877, **2**, 193) obtained from orthochlorobenzenesulphonamide, can be prepared by the action of fuming sulphuric acid on chlorobenzene. The chloride of this acid forms white crystals, which melt at 29° . On nitration with a mixture of equal parts of fuming sulphuric and nitric acids, orthochlorobenzenesulphonic chloride is converted into orthochloronitrobenzenesulphonic chloride, a yellow oily liquid. On reduction with tin and hydrochloric acid a poor yield of chloramidophenyl-mercaptan hydrochloride is obtained. It crystallises in flesh-coloured needles. The free base melts at 129° , and appears to be identical with metachloramidophenyl-mercaptan, in which case the SH group occupies a para-position to the amido-group, and the ortho-position to the chlorine-atom.

No bases were produced by the action of organic acids or acid chlorides on this substance. W. C. W.

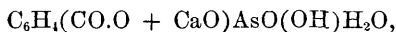
Hydrazobenzenetetrasulphonic Acid. By J. LIMPRICHT (*Ber.*, **14**, 1543—1544).—Wilsing has obtained hydrazobenzenetetrasulphonic acid by heating hydrazobenzenedisulphonic acid from metanitrobenzenesulphonic acid with fuming sulphuric acid for 10 minutes. The acid solution is poured into water, and neutralised with milk of lime; the filtrate from the precipitated calcium sulphate is concentrated and allowed to cool, when yellowish crystals of the calcium salt are deposited. A further yield of the salt is obtained by adding alcohol to the mother-liquor. All the salts of hydrazobenzenetetrasulphonic acid, with the exception of the lead salt, are freely soluble in water, and sparingly soluble in alcohol. The *barium* salt, $\text{Ba}_2\text{C}_{12}\text{H}_8\text{N}_2\text{S}_4\text{O}_{12} + 14\text{H}_2\text{O}$, crystallises in large colourless prisms. The *potassium* and *sodium* salts are precipitated from their aqueous solutions in needle-shaped crystals, on the addition of alcohol. Neutral solutions give a white precipitate with basic acetate of lead, and reduce silver salts.

Hydrazobenzenetetrasulphonic acid is a thick syrupy liquid, and forms microscopic crystals when left over strong sulphuric acid. No satisfactory results were obtained by the action of phosphorus pentachloride on the potassium salt, nor by treating the acid with bromine or nitrous acid. W. C. W.

Benzarsinic Acid and its Derivatives. By W. LA COSTE (*Annalen*, **208**, 1—36).—Part I. *Monobenzarsinic Acid*.—The author at the outset alludes to the stability of the organic derivatives of arsenic acid, and the readiness with which the methyl group of toluene compounds is oxidised into the corresponding carboxyl group. The starting point of the research was paratolylarsinic acid, $\text{C}_6\text{H}_4\text{AsOH}_2$ (Abstr., 1880, 397), which, when heated at 60° for several days with alkaline permanganate, is converted into a tripotassium salt of benzarsinic acid. By the action of acetic acid, this yields an acid dihydrogen potassium salt, which gives free monobenzarsinic acid,



(cf. Abstracts, this vol., 68), when dissolved in hot concentrated hydrochloric acid. This acid crystallises in colourless transparent tables, sparingly soluble in cold alcohol and acetic acid, readily soluble in hot alcohol, and alkaline hydroxides and carbonates. The crystals of the acid lose their transparency when heated, giving off a molecule of water, and being converted into an anhydride, $\text{COOH.C}_6\text{H}_4.\text{AsO}_2$, which is completely decomposed at 230° . Benzarsinic acid forms salts in which the hydrogen, not only of the carboxyl group, but also of the hydroxyl group is replaced by metals. The *dihydrogen potassium salt*, $\text{COOK.C}_6\text{H}_4\text{AsO}(\text{OH})_2 + \text{COOH.C}_6\text{H}_4.\text{AsO}(\text{OH})_2$, crystallises in long transparent tables of triclinic form. The *calcium* salt,



is obtained as a leafy precipitate by decomposing a neutral solution of the sodium salt with calcium chloride. The *silver* salt,



is a white amorphous precipitate insoluble in water, but perfectly soluble in ammonia and nitric acid. By heating the silver salt to 100° with methyl iodide, the *monomethyl* salt, $\text{COOMe.C}_6\text{H}_4.\text{AsO}(\text{OH})_2$, is obtained as a colourless crystalline mass, which can be saponified by water or alkalis. On treating benzarsinic acid with hydriodic acid and a small quantity of amorphous phosphorus, a golden precipitate of *benzarseniodide*, $\text{COOH.C}_6\text{H}_4.\text{AsI}_2$, separates out. This compound crystallises in long golden needles (m. p. 153°), easily soluble in alcohol and ether; and when heated with silver chloride, forms the corresponding chlorine compound. Benzarseniodide dissolves in sodium carbonate with evolution of carbonic anhydride and formation of *benzarsenious acid*, $\text{COOH.C}_6\text{H}_4.\text{As}(\text{OH})_2$. This acid crystallises in colourless needles, which loses its water of hydration at 145 — 160° , with formation of an *anhydride*, $\text{COOH.C}_6\text{H}_4.\text{AsO}$.

Benzarsenious acid gives salts in which only the hydrogen of the carboxyl group is replaced by hydrogen. The *calcium* salt forms glistening pearly leaflets; the *silver* salt separates out as a sparingly soluble precipitate.

Part II. *Dibenzarsinic Acid*.—In order to obtain this acid, the author isolated and investigated the *paraditolyarsenic* compound. *Paraditolyarsenious chloride*, $\text{As}(\text{C}_6\text{H}_4\text{Me})_2\text{Cl}$, is prepared by the action of mercury-ditolyl on an excess of monotolyarsenious chloride. Owing to the readiness with which the ditolyl compound splits up into the monotolyarsenious chloride and tritolyarsine, the crude product of reaction is treated with a solution of sodium carbonate, which converts the dichloride into the oxide, whilst the ditolyl compound is left unattacked. The ditolyarsenious chloride is a golden-coloured oil, analogous in properties to the corresponding diphenyl compound; it does not, however, solidify even at a temperature of a freezing mixture. On boiling the chloride with an excess of alcoholic potash, it is converted into *paratolyarsenious oxide*, $\text{OAs}_2(\text{C}_6\text{H}_4\text{Me})_4$, which crystallises in silky needles (m. p. 98°). Ditolyarsenious chloride absorbs chlorine, with formation of ditolyarsenious trichloride, which can be converted by gradual addition of water into *paraditolyarsinic acid*, $\text{As}(\text{C}_6\text{H}_4\text{Me})_2\text{O.OH}$. This acid forms small horny crystals (m. p. 167°), soluble in water and dilute hydrochloric acid, its alkali and alkaline earth salts are readily soluble in water; the silver salt is a sparingly soluble white precipitate. Alkaline permanganate oxidises ditolyarsinic acid to *dibenzarsinic acid*,



which separates out from hydrochloric acid in the form of large glistening leaflets. The salts of this acid do not crystallise readily, the alkali salts are easily soluble in water and alcohol, the salts of the heavy metal are only sparingly soluble in water. Although it would appear that dibenzarsinic acid is a tribasic acid, yet the author has succeeded only in obtaining salts, in which all the hydrogen of the carboxyl group is replaced. The dimethyl salt, $\text{As}(\text{C}_6\text{H}_4.\text{COOMe})_2\text{O.OH}$, forms a crystalline, golden-yellow crust, which melts above 280° without decomposition. By heating dibenzarsinic acid with concentrated

hydriodic acid and amorphous phosphorus, it is converted into *dibenzarsenious iodide*, $\text{As}(\text{C}_6\text{H}_4.\text{COOH})_2\text{I}$, a crystalline powder (m. p. above 280°), soluble in alcohol, ether, and chloroform.

Dibenzarsenious iodide dissolves in sodium carbonate solution, with evolution of carbonic anhydride and formation of dibenzarsenious acid, $\text{As}(\text{C}_6\text{H}_4.\text{COOH})_2.\text{OH}$, a white crystalline compound sparingly soluble in water and dilute mineral acids.

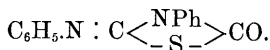
Part III. *Tribenzarsinic Acid*.—The author has already shown (Abstr., 1880, 397), that on heating monotoylarsenious oxide to 360° it splits up into arsenious oxide and tritolyarsine; the latter can be separated from the hard crust of the oxide by solution in ether. *Tritolyarsine* forms colourless crystals (m. p. 145° , not 130° , as formerly stated by the author), which can be heated to 360° without decomposition. Tritolyarsine does not readily take up chlorine; the dichloride is best prepared by passing chlorine into a chloroform solution of tritolyarsine; it is a golden-yellow oil, which, after standing for a long time, solidifies to a white crystalline mass (m. p. 214°). As the preparation of tritolyarsenious oxide or hydroxide presented some difficulty, tritolyarsine was oxidised directly by alkaline permanganate into *tribenzarsinic acid*, $\text{As}(\text{C}_6\text{H}_4.\text{COOH})_3(\text{OH})_2$. This acid separates out from hydrochloric acid as a white voluminous precipitate, which loses water when heated, and decomposes at a higher temperature. It appears that this acid generally acts as a tribasic acid, although the silver salt had probably the formula $\text{As}(\text{C}_6\text{H}_4.\text{COOAg})_3(\text{OAg}).\text{OH}$. Tribenzarsinic acid can be reduced by hydriodic acid to *tribenzarsenious acid*, $\text{As}(\text{C}_6\text{H}_4.\text{COOH})_3$; the yield is however small. This latter compound separates out from an ethereal solution in large colourless needles; in its constitution it is analogous to triglycollamic acid, $\text{N}(\text{CH}_2.\text{COOH})_3$. The *sodium* salt crystallises in short needles; the *silver* salt is a white voluminous precipitate.

Part IV. *Oxidation of Dimethyl- and Ethyl-arsinic Acids*.—The author endeavoured to convert cacodylic acid into the corresponding dicarboxylic acid by oxidation with alkaline permanganate, but the reaction failed; the same happened with ethylarsinic acid. The author recommends the action of mercury diethyl on arsenic trichloride as a ready method for obtaining ethylarsenious dichloride.

V. H. V.

Action of Carbonyl Chloride, and of Alcoholic Bromides, &c., on Substituted Thiocarbamides. By W. WILL (Ber., 14, 1485—1492).—When a solution of carbonyl chloride in benzene is added in excess to a thiocarbanilide suspended in benzene, complete solution ensues, hydrochloric acid is evolved after a time, and a precipitate is formed, which consists of carbanilide, thiocarbanilide, and triphenylguanidine. The precipitate is washed with cold ether. On evaporating the filtrate, lustrous prisms (m. p. 87°) of carbonylthiocarbanilide, $\text{C}_{14}\text{H}_{10}\text{N}_2\text{SO}$, are deposited. This substance dissolves freely in ether, benzene, and carbon bisulphide. On boiling the alcoholic solution with hydrochloric acid or sodium hydroxide, or on boiling with water, carbanilide, sulphuretted hydrogen, and carbonic acid are formed. By the action of alcoholic ammonia, the carbonylthio-

carbanilide is split up into thiocarbanilide and urea, and by aniline it is converted into carbanilide and thiocarbanilide. When heated above its melting point, this substance suddenly splits up into carbodiphenylimide and carbonyl sulphide. Carbonyl-thiocarbanilide may probably be represented by the formula—



Action of Carbonyl Chloride on Ditolylthiocarbamide.—Carbonyl-thiocarbotoluidide, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{SO}$, is obtained in long silky needles (m. p. 116°), when ditolylthiocarbamide is substituted for thiocarbanilide in the first experiment. It is sparingly soluble in cold alcohol, but dissolves freely in ether and benzene. This compound is decomposed by alcoholic potash or hydrochloric acid, forming carbotoluidide, and by alcoholic ammonia, yielding urea and thiocarbotoluidide. Heated at 100° , it slowly splits up into carbonyl sulphide and carboditolyimide, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{SO}$; the change takes place more rapidly at temperatures above the melting point of the substance. The base crystallises in thick prisms (m. p. 60°), soluble in benzene and ether. It boils at 230° . The hydrochloride crystallises in needles. On boiling with water, dilute hydrochloric acid, or sodium hydroxide, it yields ditolyl-carbamide.

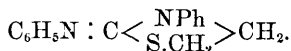
Phenyl-ditolyguanide, formed by the action of aniline on carboditolyimide, crystallises in needles.

Carbonyl chloride also acts on monophenylthiocarbamide, diallylthiocarbamide, &c., at the ordinary temperature. Carbonyl sulphide has no action on thiocarbanilide. Carbanilide is not attacked either by carbonyl chloride or by carbonyl sulphide.

Action of Methyl and Ethyl Iodides on Thiocarbanilide.—On heating methyl iodide and thiocarbanilide in molecular proportions in a flask fitted with an upright condenser, a crystalline hydriodide, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}\cdot\text{HI}$, is obtained, which is sparingly soluble in cold water. The free base is soluble in alcohol. It melts at 110° , and at a higher temperature decomposes into mercaptan and carbodiphenylimide. The base is decomposed by boiling with potassium hydroxide, forming mercaptan and carbanilide. Heated with hydrochloric acid at 150° , it splits up into aniline and methyl mercaptan.

The corresponding ethyl base, $\text{C}_{15}\text{H}_{16}\text{N}_2\text{S}$, melts at 79° , and has the constitution $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}(\text{NPhH}) : \text{NPh}$.

Action of Ethylene Bromide on Thiocarbanilide.—On heating ethylene bromide and thiocarbanilide, hydrobromic acid is evolved, and a residue remains, which is soluble in water. Sodium hydroxide precipitates hydrothiodiphenylhydantoin from the aqueous solution of this product. The base crystallises in plates (m. p. 136°). It is not decomposed by boiling with hydrochloric acid or alcoholic potash, and it can be distilled without decomposition. The constitution of this compound may be represented as



W. C. W.

Constitution of Diphenyl Derivatives. By G. SCHULTZ (*Annalen*, **207**, 361—368).—The author gives a list of all diphenyl derivatives in which the positions of the groups of atoms replacing hydrogen are wholly or partially known. He shows that the same rules which have previously been observed with benzene compounds with regard to melting points, solubilities, and boiling points, also obtain in the case of diphenyl derivatives. The ortho-compounds are more soluble, have a lower melting point, and generally a lower boiling point, than the corresponding para-compounds. Chlorine compounds melt lower than bromine ones, and these again lower than those containing iodine; also methylic higher than ethylic ethers. Each successive atom of bromine entering into combination raises the boiling point about 60° . The same variations in melting point exhibited by the nitro-, azo-, azoxy-, hydrazo-, and amido-benzene compounds are also shown by the diphenyl derivatives. On the replacement of oxygen in the nitro-groups, in the case of benzene compounds, the melting point increases until the azo-compound is reached, the hydrazo-compounds melting lower than the azo- and even than the azoxy- (hydrosulphuric acid being excepted), and the amido-compounds even lower than the corresponding nitro-bodies. The diphenyl base of the series, however, has a higher melting point. J. I. W.

Diphenyl Bases. By G. SCHULTZ (*Annalen*, **207**, 311—319).—*The molecular changes which hydrazo-compounds undergo when subjected to the action of mineral acids.*—By treating azobenzene with sulphuretted hydrogen and acting on the product so obtained with sulphuric acid, Zinin obtained a body which he called benzidine. He considered that it was formed directly from azobenzene; but Hofmann showed that hydrazobenzene is first formed, and this, when treated with sulphuric acid, yields benzidine. Fittig soon afterwards found that by reducing dinitro-diphenyl, a diamidodiphenyl is formed, which bears a close resemblance to benzidine. Griess next showed that diphenyl can be obtained by boiling tetrazo-diphenyl sulphate, derived from benzidine, with alcohol. The author (*Annalen*, **174**, 227) proved that the diamido-diphenyls obtained from hydrazobenzene and dinitro-diphenyl are identical.

The conversion of hydrazobenzene, Ph.NH.NH.Ph. into diamido-diphenyl, $\text{NH}_2.\text{C}_6\text{H}_4.\text{C}_6\text{H}_4.\text{NH}_2$, is one of the most striking examples of molecular re-arrangement. The corresponding chlorine and bromine compounds have been prepared from dichloro- and dibromo-hydrazobenzene. Griess states (*Annalen*, **154**, 213) that when an ammoniacal solution of azobenzenemonosulphonic acid is treated with sulphuretted hydrogen, it yields benzidinesulphonic acid; the author shows that the substance is probably parahydrazobenzenesulphonic acid. It is remarkable that the acid is converted into benzidine by the action of ammonia, whilst the other hydrazo-compounds are only decomposed by a mineral acid.

The three symmetrical diamidoditolyls are formed from the hydrazo-compounds in a similar manner to the diamidodiphenyls; not one of them, however, has yet been directly prepared from, or converted into, ditolyl.

By boiling with hydrochloric acid, metahydrazobenzoic acid, $\text{COOH.C}_6\text{H}_4.\text{NH.NH.C}_6\text{H}_4.\text{COOH}$, is converted into diamidodiphenyl-dicarboxylic acid, $\text{COOH.}(\text{NH}_2)\text{C}_6\text{H}_3.\text{C}_6\text{H}_3(\text{NH}_2).\text{COOH}$. Up to the present time no azo- or hydrazo-compounds in the fatty series have been prepared; it is, however, probable that such bodies can exist, and that they would exhibit properties similar to those of the aromatic ones, so that one would expect that one of the so-called mixed azo-compounds containing aromatic and fatty residues side by side, the amidoethaneazobenzenesulphonic acid of Kappeler, would be converted into the benzidine compound, diamidoethylamidobenzene-sulphonic acid.

It is noticeable that the molecular change does not take place with equal readiness in all cases of hydrazo-bodies; for while azo- and hydrazo-benzene are easily transformed into benzidine by the action of a mineral acid, the corresponding toluene compounds are extremely difficult to attack. Although dichlorhydrazobenzene, prepared from meta-chloronitrobenzene, easily yields dichloro-diamido-diphenyl when heated with hydrochloric acid, dichlorhydrazobenzene prepared from para-chloronitrobenzene, according to Calm and Heumann, yields only a mixture of para-dichlorazobenzene and para-chloraniline. The bromine derivative behaves in the same manner.

Boiling hydrochloric acid, according to Andreae (*J. pr. Chem.*, **21**, 318), converts dinitro-orthhydrazophenetol into dinitro-orthazophenetol and orthamido-para-nitrophenetol. The hydrogen atoms, which occupy the para- or ortho-position with regard to the amido- or hydroxyl-groups, appear to be remarkably variable. For instance, aniline and paratoluidine yield pararosaniline; in which case, that atom of hydrogen is displaced which is in the para-position with respect to the amido-group. In some cases the para- and ortho-compounds are produced almost in equal quantities: for instance, in the formation of salicaldehyde and paroxybenzaldehyde from phenol, chloroform, and sodium hydroxide. In other cases, the ortho-compound is produced in greater quantity or by itself.

The same rule appears to apply in the case of the so-called molecular re-arrangements, when an isomeric body is produced, not by an internal change in one molecule, but by the action of similar molecules on one another. If diazoamidobenzene is acted on with aniline hydrochloride, its isomeride paramidoazobenzene is formed: the latter is decomposed by reducing agents into aniline and para-diamidobenzene. Amidoazobenzene can also be obtained directly from aniline and nitrous acid, diazoamidobenzene being first formed. In a similar manner orthamidotoluene and metamidotoluene, on treatment by nitrous acid, yield orthotoluene, azoparamidometatoluene, and metatolueneazoparamidoorthotoluene. On the other hand, paramidotoluene does not give amidazotoluene, but paradiazoamidotoluene, which does not exhibit any re-arrangement, because that carbon-atom which assumes the para-position with respect to the one combined with the NH-group, is in connection with a methyl-group and not a hydrogen-atom. The formation of benzidine from hydrazobenzene by the action of hydrochloric acid affords another example of the replace-

ment of the hydrogen-atom, which is in the para-position to the NH-group.

From the foregoing examples, the author deduces the general rule, that in the molecular re-arrangement of diazoamido- and hydrazobodies, principally those hydrogen-atoms occupying the para-position with regard to the NH-groups are removed and replaced by groups of atoms, amido-compounds being at the same time formed. If, however, these hydrogen-atoms are already replaced by other elements or groups, the re-arrangement is not necessarily checked; for the formation of a tolidine from parazotoluene, and of orthamido-paramidodiphenyl, show most clearly that in these molecular changes, bases, whose amido-groups are not necessarily in the para-position to the replaced hydrogen-atoms, can be formed.

J. I. W.

Benzidine (α -Diamidodiphenyl). By H. SCHMIDT and G. SCHULTZ (*Annalen*, **207**, 320—347).—The benzidine obtained from hydrazobenzene with hydrochloric acid or from dinitrodiphenyl with reducing agents, or from diamidodiphenic acid with lime, is diparamidodiphenyl (Schultz, *Annalen*, **174**, 227), because it can be obtained by reducing paranitroparamidodiphenyl, $\text{NO}_2(4) \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2(4)$. The latter body is a dipara-compound, because it can be converted into paranitroparabromodiphenyl, which, on oxidation with chromic acid, yields paranitrobenzoic and parabromobenzoic acids.

Diacetylhydrazobenzene, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$, or $\text{NPh}\bar{\text{Ac}} \cdot \text{NPh}\bar{\text{Ac}}$.—This compound is prepared by boiling hydrazobenzene for several hours with acetic anhydride. The crude product is then treated with water, and the residue crystallised from alcohol. It is only slightly soluble in cold water, but more easily in hot. It dissolves readily in alcohol, ether, and acetic acid, and crystallises from dilute alcohol in large yellowish crystals (m. p. 105°). When heated above its melting point, it decomposes. It is scarcely attacked by boiling hydrochloric acid, but concentrated sulphuric acid converts it into benzidine.

The authors prepare azobenzene in the following manner:—One part of nitrobenzene is dissolved in 9 volumes of alcohol and heated for several hours with 1 part of potassium hydroxide until the mixture boils quietly. The alcohol, aniline, and unattacked nitrobenzene are then distilled off, and the black residue poured into water. After standing for several days, azoxybenzene, mixed with aniline and nitrobenzene, separates out. The crystals, after drying, are treated with alcohol containing a small quantity of fuming nitric acid. The yield of azoxybenzene is about 40 per cent. of the nitrobenzene employed.

In order to convert the azoxybenzene into azobenzene, the authors distil it with iron filings. A yield of 72.5 per cent. is obtained in this manner. To prepare benzidine and diphenylene from azobenzene, it is dissolved in alcoholic ammonia and treated with sulphuretted hydrogen. On concentrating the solution, hydrazobenzene crystallises out. After drying, it is converted into the mixed hydrochlorides, by heating with hydrochloric acid. On addition of sulphuric acid, the less soluble benzidine sulphate is precipitated, while the corresponding diphenylene salt remains in solution. In this

manner, 20 grams of azobenzene yield 18 grams of benzidine sulphate. It is not, however, necessary to prepare hydrazobenzene; for if an alcoholic solution of azobenzene is treated with zinc chloride and hydrochloric acid, the mixed bases are directly obtained. The filtrate from the benzidine sulphate is evaporated, mixed with an excess of potassium hydroxide, and extracted with ether. By fractionating, the oil can be separated into aniline and β -diamidodiphenyl (b. p. 363°). Azobenzene yields 18.5 per cent. of aniline and 18.3 per cent. of β -diamidodiphenyl.

γ -Diphenol obtained from Benzidine. — If an aqueous solution of tetrazodiphenyl sulphate obtained from benzidine is boiled for some time, nitrogen is evolved and a brownish-yellow powder is precipitated, consisting principally of dipara-oxydiphenyl. By treatment with alcohol and subsequent distillation, it can easily be separated from bye-products; but the formation of these bodies can be greatly lessened by the addition of a small quantity of urea or alcohol to the boiling solution. The diphenol crystallises from alcohol in white glistening plates, or tufts of needles, which are only slightly soluble in water and in benzene, but easily in alcohol or ether. It is dissolved by alkalis, and reprecipitated on addition of acids. On heating, it begins to turn brown at 250° , melts at 272° , and boils at 360° . It dissolves in concentrated sulphuric acid, to which it imparts a greenish tinge. In presence of nitrous fumes, the solution becomes blue. The nitro-derivative dyes wool a light yellow colour. On heating the diphenol with nitric acid, it is converted into picric and oxalic acids.

Diacetyl γ -diphenol, $C_{12}H_8(O\cdot\text{Ac})_2$, is obtained by boiling the diphenol with acetic anhydride. It melts at 159 – 160° , is easily soluble in alcohol and glacial acetic acid, and crystallises in long needles. It dissolves in crude sulphuric acid with a blue colour.

γ -Diphenol from Diphenyldisulphonic Acid. — The disulphonic acid is obtained by heating 50 grams of diphenyl with 100 grams of ordinary and 50 grams of fuming sulphuric acid. The potassium salt, when fused with potassium hydroxide, yields a diphenol which melts at 272° , has the same crystalline form, and behaves in the same manner with reagents as the preceding compound. It yields a similar acetyl compound, and is in all respects identical with the diphenol obtained from benzidine. Its vapour-density was found by the authors to be 6.50 (cal. = 6.44).

On treating γ -diphenol with phosphorus pentachloride, a mixture of several substances is obtained. The authors have succeeded in isolating three. 1. A chlorinated substance, melting at 126° , soluble in alkalis. The authors suggest that it may be a trichlorodiphenyl. 2. Diparachlorodiphenyl, melting at 148° . 3. The body melting at 179° previously obtained by Döbner. The mixture of chlorinated substances is treated with water and then with a dilute solution of sodium hydroxide; after filtering, hydrochloric acid precipitates a substance which was proved not to be γ -diphenol. It melts at 126° , and distils without decomposition. It is soluble in alkalis and reprecipitated by acids. It dissolves in sulphuric acid with a green colour, which rapidly changes to violet. The residue remaining, after treating the

crude product with sodium hydroxide, is distilled, the distillate being collected in three portions, 315—333°, 333—360°, and above 360°. The first portion consists principally of diparachlorodiphenyl, identical in melting point, crystalline form, and general behaviour with that obtained directly from benzidine and diphenyl. The second portion, in addition to diparachlorodiphenyl and other chlorinated bodies easily soluble in alcohol, contains a body (m. p. 179°) little soluble in alcohol, which is identical with that obtained by Döbner. It boils much above 360°. It sublimes in long silky needles. The authors find that it is pentachlorodiphenyl, $C_{12}H_5Cl_5$.

γ-Diphenol from Dioxyphenylbenzoic Acid.—By heating diphenylene-ketone with a mixture of ordinary and fuming sulphuric acid at 250—260°, diphenyleneketonedisulphonic acid is formed. On fusing the potassium salt with potassium hydroxide and decomposing the product with sulphuric acid, dihydroxyphenylbenzoic acid (m. p. 270°) is obtained. On distilling with lime, it yields a diphenol which is identical with those obtained from benzidine and diphenyldisulphonic acid. Dihydroxyphenylbenzoic acid is therefore dipara-hydroxyortho-carboxyldiphenyl.

Acetylparamido-paranitrodiphenyl, $C_{14}H_{11}N_2O_3$, forms bright yellow needles, melting at 264°.

Paranitro-parahydroxydiphenyl, $C_{12}H_8(NO_2)(OH)$, is formed by treating paranitro-paramidodiphenyl with nitrous acid. It crystallises in needles (m. p. 170°).
J. I. W.

Diphenylene (β -Diamidodiphenyl). By G. SCHULTZ, H. SCHMIDT, and H. STRASSER (*Annalen*, **207**, 348—360).—By acting on diphenyl with an excess of concentrated nitric acid, two isomeric dinitrodiphenyls are obtained. They can be separated by means of the difference in their solubilities in alcohol. The least soluble is diparanitrodiphenyl (m. p. 233°), which, on reduction, yields benzidine. The other is isodinitrodiphenyl (m. p. 93·5°), which the authors show is a para-ortho-compound, containing the two nitro-groups in different benzene nuclei. On reduction with sulphuretted hydrogen, it yields iso-amidonitrodiphenyl, which, on treatment with tin and hydrochloric acid, gives a diamidodiphenyl resembling in all respects that which is produced along with benzidine from hydrazobenzene. The authors propose to call it diphenylene or β -diamidodiphenyl. The mode of preparing it from hydrazobenzene is described in the preceding Abstract. In order to obtain the base from diphenyl, it is necessary first to prepare iso-dinitrodiphenyl and then iso-amidonitrodiphenyl.

Iso-dinitrodiphenyl, $NO_2.C_6H_4.C_6H_4.NO_2 = [2:1:4]$, forms small yellowish needles belonging to the regular system.

Iso-amidonitrodiphenyl, $NO_2.C_6H_4.C_6H_4.NH_2$, forms regular reddish-brown crystals, and, on treatment with nitrous acid, yields isonitroxidiphenyl (m. p. 138°), crystallising in small yellow needles.

Isobromonitro-diphenyl, $NO_2.C_6H_4.C_6H_4Br$, is formed, together with parabromo-paranitrodiphenyl, on treating parabromodiphenyl with concentrated nitric acid. It is also obtained when the perbromide of the diazo-compound, prepared from iso-amidonitrodiphenyl, is boiled with alcohol. It crystallises from alcohol in glistening plates (m. p. 65°). On

oxidation with chromic acid, it yields parabromobenzoic acid. One nitro-group, therefore, of iso-dinitrodiphenyl occupies the para-position. The authors show that the other is in the ortho-position, because iso-dinitrodiphenyl can be obtained by nitrating mononitrodiphenyl, and the iso-bromodiphenyl derived from the latter yields orthobromobenzoic acid on oxidation.

Orthonitrodiphenyl, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_5$, is produced, together with paranitrodiphenyl, when diphenyl is treated with concentrated nitric acid. It crystallises from alcohol in large plates (m. p. 370°).

Isobromodiphenyl, $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}_6\text{H}_5$, is prepared by boiling iso-diazodiphenyl perbromide with alcohol, and afterwards distilling with steam. It forms a clear oil (b. p. $296-298^\circ$), smelling like oranges. It solidifies at -20° . On oxidation, it yields orthobromobenzoic acid (m. p. 158°).

Diphenylene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 = [2:1:4]$, is best prepared by treating azobenzene or iso-amidonitrodiphenyl with stannous chloride. It is almost insoluble in water, but dissolves easily in alcohol or ether. It crystallises in long needles (m. p. 45° , b. p. 363°), which gradually decompose in the air. On treatment with acetic acid, it yields diacetyldiphenylene, which crystallises from alcohol in needles (m. p. 202°). *Diphenylene sulphate* is very soluble in water, crystallising therefrom in hard transparent prisms, arranged in groups. The corresponding benzidine salt is almost insoluble in water. The *mono-hydrochloride*, $\text{C}_{12}\text{H}_8(\text{NH}_2)_2 \cdot \text{HCl}$, crystallises from water in plates. Another salt, which is probably the dihydrochloride, is very soluble in water, and can only be obtained by allowing the aqueous solution to stand for several weeks, with a large excess of fuming hydrochloric acid. It forms long colourless needles, very soluble in water; the solution, however, gives no precipitate with platinum chloride.

δ -Diphenol obtained from diphenylene.—If alcohol or ether is added to a solution of diphenylene sulphate saturated with nitrous acid, tetrazodiphenyl is precipitated as a brown oil. On boiling this with water, nitrogen is evolved, and a resinous product separates out. By extracting the filtrate with ether, δ -diphenol may be obtained in brown crystals (m. p. 342°). On boiling with acetic anhydride, it is converted into di-acetyldiphenol, $\text{C}_{12}\text{H}_8(\text{OAc})_2$, which crystallises from alcohol in glistening plates (m. p. 94°). Pure concentrated sulphuric acid dissolves δ -diphenol without any coloration; but crude acid gives a blue colour. Concentrated nitric acid converts it into a yellow nitro-body.

δ -Diphenol from Phenolparasulphonic Acid.—The authors show that the diphenol obtained by Zincke by fusing the potassium salt of phenolparasulphonic acid with potassium hydroxide is identical with the δ -diphenol here described. It yields an acetyl compound, melting at 94° . The diphenol obtained by Herzig by fusing phenolortho-sulphonic acid with potassium hydroxide is also identical with that obtained from diphenylene. J. I. W.

Preparation of Triphenylmethane, Tetraphenylethylene, Tetratolylethylene, &c. By H. SCHWARZ (*Ber.*, **14**, 1516—1532).—Triphenylmethane can be easily prepared by adding 15 to 20 grams of

aluminium chloride in three or four portions to a mixture of 100 grams of benzene and 70 grams of chloroform. The mixture must be cooled at the beginning of the operation, but when the action slackens, it may be gently warmed on a water-bath. Water is then slowly added to the product until the evolution of hydrochloric acid ceases, the solution is shaken up with ether, and the ethereal extract is distilled after having been previously dried over potassium hydroxide and calcium chloride. That portion of the distillate which passes over between 280° and 340° is chiefly triphenylmethane. When the distillate no longer crystallises on the addition of benzene, it is collected apart and redistilled, by which means it is separated into triphenylmethane and tetraphenylethylene. On mixing the distillate boiling between 280° and 340° with 50 per cent. of benzene, the compound $C_{19}H_{15} + C_6H_6$ is deposited as a crystalline mass. This is pressed to remove the mother-liquor, and purified by recrystallisation from hot benzene or hot alcohol. The benzene-compound melts at 76° , and begins to boil at 80° . After the benzene has been expelled, the triphenylmethane melts at 92.5° and boils at 330° .

The compound $C_{19}H_{15}Br$ is obtained by exposing a solution of bromine and triphenylmethane in carbon bisulphide to sunlight. It melts at 152° and begins to decompose at 200° , forming diphenylphenylenemethane (m. p. 144°). When a solution of the bromide in hot glacial acetic acid is poured into water, it is converted into the carbinol (m. p. 157°). Triphenylmethane is also formed by the action of methylene dichloride or benzyl trichloride on benzene.

Tetraphenylethylene, $C_{26}H_{20}$, which has been described by Behr (*Ber.*, **3**, 751), Stædel (*Ber.*, **9**, 562), and Engler and Bethge (*Ber.*, **7**, 1128), is obtained in the preparation of triphenylmethane from chloroform and benzene, from the portion boiling at 340° . It is easily separated from triphenylmethane, since it does not unite with benzene to form a crystalline compound. It crystallises in rhombic plates (m. p. 204°), of a pale straw colour, which are soluble in glacial acetic acid, chloroform, warm carbon bisulphide, and hot alcohol.

By the action of aluminium chloride on a mixture of toluene and chloroform, a heavy oil is obtained (boiling between 240° and 350°), which deposits small crystalline plates of *tetratolyethylene*, $(C_7H_7)_2C:C(C_7H_7)_2$. This substance resembles tetraphenylethylene in many respects, but differs from it in its higher melting point (215°), and by being less soluble in benzene, &c.

The oil (b. p. 298°) from which these crystals were deposited appears to be either a condensation-product of toluene $n(C_7H_8)$, or perhaps ditolylmethane, $CH_2(C_7H_7)_2$.

Tetraxylylmethylene, $C_2(C_8H_8)_4$, prepared by the action of aluminium chloride on a mixture of xylene and chloroform, crystallises in yellow plates (m. p. 245°), which are less soluble than tetratolyethylene.

An intense greenish-blue coloration is produced by the addition of dry aluminium chloride to a solution of naphthalene in chloroform.

W. C. W.

Products Accompanying Dibenzyl in the Aluminium Chloride Reaction. By R. D. SILVA (*Bull. Soc. Chim.* [2], **36**, 24—26).—By the action of anhydrous aluminium chloride on benzene and

ethylene chloride (Friedel and Crafts' process), there is obtained a crude product, separable into two distinct fractions, one boiling from 80—280°, the other above 280°. The former contains small quantities of ethylbenzene, produced by some reducing action of the aluminium chloride; in the latter is a fraction boiling about 340°, probably triphenylethane.

V. H. V.

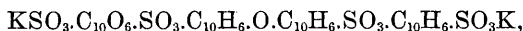
Action of Phosphorus Pentachloride on β -Naphtholsulphonic Acid. By A. CLAUS and O. ZIMMERMANN (*Ber.*, **14**, 1477—1485).—

The products of the action of phosphorus pentachloride on potassium β -naphthol sulphonate, vary with the temperature at which the reaction takes place, and with the relative proportions of the reagents.

1. The salt, $\text{HO.C}_{10}\text{H}_6.\text{SO}_3\text{C}_{10}\text{H}_6.\text{SO}_3\text{K}$, is formed by heating 1 molecule of potassium naphtholsulphonate with 2 mols. phosphorus pentachloride at 100° for two hours. The crude product is shaken up with water and ether, and the ethereal extract is boiled with water until a clear solution is obtained.

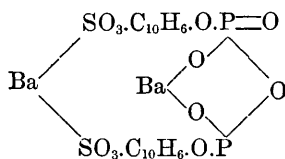
2. *Potassium β -naphthoetherdisulphonate*, $\text{KSO}_3.\text{C}_{10}\text{H}_6.\text{O.C}_{10}\text{H}_6.\text{SO}_3\text{K}$, formed simultaneously with salt (1) is insoluble in cold water. The potassium salt obtained by neutralisation with potassium carbonate, is deposited from an alcoholic solution in colourless plates, which are sparingly soluble in water. The free acid obtained by decomposing its silver salt with hydrochloric acid, dissolves in alcohol, ether and water. It is deposited from a hot aqueous solution as a transparent gelatinous mass. On boiling with an excess of alkali, the acid is converted into β -naphtholsulphonate.

3. *Potassium tetranhydronaphtholsulphonate*,



is prepared by heating at 150° phosphorus pentachloride (2 mols.) with potassium naphtholsulphonate (1 mol.); the product is washed with cold water, then boiled with hot water, and the solution neutralised with potassium carbonate. The potassium salt is deposited from the aqueous solution as a gelatinous mass soluble in alcohol. The mother-liquor contains the potassium salt of *chloronaphthol ether phosphoric acid*.

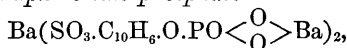
4. *Barium etherpyrophosphoric dinaphtholsulphonate*—



is obtained by heating equal numbers of molecules of phosphoric pentachloride and potassium β -naphtholsulphonate at 100°. The product is washed with cold water, the residue is dissolved in hot water, and the hot solution neutralised with potassium carbonate; on cooling it deposits salt (1). The mother-liquor from these crystals is acidified with sulphuric acid, potassium sulphate removed by crystallisation, and the free acid neutralised with barium carbonate. On the addition of alcohol to the concentrated solution, the barium salt (4) is deposited in crystalline

scales. The salt is decomposed into phosphate and β -naphtholsulphonate by boiling with free alkalis.

5. *Barium sulphonaphthoetherphosphate*—



is separated from the products of the action of 2 mols. phosphorus pentachloride on 1 mol. potassium naphtholsulphonate, by a process similar to that employed for isolating the above salt. It is, however, unnecessary to add alcohol in order to precipitate this salt, as it is sparingly soluble in cold water, and is consequently carried down with the barium sulphate, from which it is separated by extraction with hot water. It is also decomposed into phosphate and β -naphtholsulphonate by boiling with potash.

6. *Chlornaphthoetherphosphoric acid* is deposited in small lustrous plates, m. p. 205° , on the addition of hydrochloric acid to a hot aqueous solution of its potassium salt. The crystals are soluble in hot water and alcohol: on boiling with alkalis the acid is split up into phosphoric acid and chlornaphthol.

Dichloronaphthalene, $\text{C}_{10}\text{H}_6\text{Cl}_2$, is prepared by heating a mixture of phosphorus pentachloride (3 mols.) and potassium β -naphtholsulphonate, for five hours in an oil-bath at 165° . On distilling the product in a current of steam, the dichloride is found in the distillate, and *chlornaphthol* remains. This dichloronaphthalene is identical with the ϵ -dichloronaphthalene, which Clève (*Bull. Soc. Chim.* [2], **26**, 244, *Jahresb.*, 1876, 405) obtained by the action of phosphorus pentachloride on β -naphthalenedisulphonic acid. It crystallises in monoclinic plates soluble in ether, chloroform, benzene, and in hot alcohol. It melts at 135° and boils at 285° , the vapour condensing in needle-shaped crystals.

Chlornaphthol, $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{OH}$, is not formed directly by the action of phosphorus pentachloride on potassium β -naphtholsulphonate, but is produced by a secondary reaction, which takes place on distilling the product in a current of steam.

It is deposited from a hot aqueous solution in white needles (m. p. 115°), which are freely soluble in alcohol and ether. W. C. W.

Action of Amines on Quinones. Part III. By T. ZINCKE (*Ber.*, **14**, 1493—1497).— β -Naphthoquinonanilide, $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{NHPh}$, is deposited in red needles or plates when aniline is added to a warm alcoholic solution of β -naphthoquinone. The crystals are sparingly soluble in benzene, toluene, and hot alcohol; they shrink together at 235° , and melt between 240° and 250° .

β -Naphthoquinonanilide dissolves in strong mineral acids, and is reprecipitated from these solutions, on dilution with water. On boiling with glacial acetic acid, it is converted into α -naphthoquinonanilide, hydroxynaphthoquinone being also formed. The β -compound plays the part of a weak acid. The *potassium* and *sodium* salts dissolve in water with a reddish-brown coloration; they are insoluble in alkalis. The *barium* and *calcium* salts are deposited from their solutions in hot alcohol in small needles of a dark-red colour, which are very slightly soluble in water. Lead, zinc, and mercury form basic compounds; the

lead salt is insoluble in alcohol, the *zinc* salt is precipitated from its alcoholic solution on dilution with water, in slender needles, and the *mercury* salt crystallises in lustrous brown plates. The *silver* salt is insoluble in alcohol and in water.

The *ethyl* salt, $C_{10}H_8EtO_2.NHPh$, forms monoclinic crystals (m. p. 104°) of a beautiful orange colour.

β -Naphthoquinonanilide is easily reduced by ammonium sulphide or by tin and hydrochloric acid. It is converted into the corresponding α -compound by boiling with alcohol containing 10 per cent. of sulphuric acid.

W. C. W.

Cananga Oil. By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], 11, 934—937).—This oil, also known as Hang-lang or Alanguilan oil, is obtained from the tree *Cananga odorata* (Unonaceæ), and according to Gal (*Compt. rend.*, 76, 1428) contains a benzoic ether. This is confirmed by the author's results, who also found it to contain acetic acid, probably as an ether, an aldehyde or ketone, and probably a phenol.

The oil is neutral and distils between 170° and 290° , above which temperature decomposition begins.

L. T. O'S.

Hydrangea Arborescens. By J. BAUR (*Pharm. J. Trans.* [3], 11, 901).—The roots of this plant contain two resins, one insoluble and the other soluble in ether. Both are insoluble in ammonia, but soluble in potassium hydroxide, giving precipitates with neutral and basic lead acetates. The insoluble resin is probably an alkaloid; with Mayer's reagent it gives a white precipitate, with iodine a brown precipitate, also precipitates with phosphomolybdic acid, cadmium chloride and platinum chloride. The roots also contain a crystalline substance, the nature of which was not determined, also tannin, gum, sugar, and colouring matter. The root leaves 4.33 per cent. of ash.

L. T. O'S.

Nerium Odorum. By H. G. GREENISH (*Pharm. J. Trans.* [3], 11, 873—875).—This plant, which is cultivated in India, is prescribed for leprosy, and is highly poisonous. With a view to ascertain the nature of the bitter principle contained in the bark and roots, the following investigation was undertaken.

The bark and wood are separately macerated with alcohol, first at the ordinary temperature, and then at 35° . This is repeated, and the filtrate from each operation evaporated, when a yellowish fatty oil separates out, which is removed by diluting the alcoholic solution with water, adding powdered bole, filtering, and evaporating.

Extract from the Bark.—Dilute sulphuric acid is added to the slightly acid filtrate, and it is then shaken first with light petroleum, and afterwards with chloroform, which assumes a brown colour, and causes a yellowish-brown oil to separate between the two liquids. On heating the oil to expel chloroform and drying over sulphuric acid, it solidifies. It is purified by digestion with chloroform and ether, then washed and dried. This substance, which the author names *neri-odorein*, is of intensely bitter taste, insoluble in chloroform, but soluble in water.

The aqueous solution is again shaken with chloroform, and the two chloroform solutions are evaporated to dryness, whereby a yellow amorphous residue of *neriodorin* is obtained, sparingly soluble in cold water, but more so in hot, easily soluble in chloroform, and of intensely bitter taste.

The aqueous solution after being agitated with chloroform, still contains some *neriodorein*.

The extract from the wood is treated in a similar manner to that of the bark, with the exception of adding sulphuric acid; it yields a small quantity of *neriodorein* and some *neriodorin* of a darker colour than that from the bark.

Neriodorein obtained as above is an intensely bitter, yellow powder, insoluble in light petroleum, ether, benzene, chloroform, carbon bisulphide, amyl alcohol, or ethyl acetate, but soluble in water, alcohol, and glacial acetic acid. All attempts to crystallise it failed, but since it passes through the septum of a dialyser, it is probably crystallisable. Concentrated sulphuric acid gives with dry *neriodorein* a reddish-brown colour, violet at the edges, which changes to dirty yellowish-brown and green. The sulphuric acid solution is coloured yellow by addition of concentrated nitric acid; Fröhde's reagent gives a dirty violet colour. Its aqueous solution, which is neutral, gives precipitates with basic lead acetate in presence of ammonia, and with tannic acid, and a slightly brown coloration with ferric chloride. It reduces Fehling's solution, and would seem to be a glucoside, as it is decomposed by hydrochloric acid, with separation of a yellow resin, leaving a yellow liquid which reduces Fehling's solution. The resin when heated with alcohol, leaves colourless needle-shaped crystals insoluble in ether, alcohol, water, and alkalis. The filtrate on evaporation leaves a yellow amorphous substance soluble in water, chloroform, and alcohol, which, with Fröhde's reagent, gives a violet colour, changing to dirty green. Neither of these substances reduces Fehling's solutions. *Neriodorein* is also decomposed by boiling with milk of lime.

Neriodorin forms a yellow varnish-like mass of intensely bitter taste, easily soluble in chloroform, with difficulty in water, alcohol, and ether, and insoluble in light petroleum, benzene, and carbon bisulphide. Its aqueous solution is neutral, and reduces Fehling's solution. When treated with hydrochloric acid, it undergoes a similar decomposition to *neriodorein*, yielding the same decomposition products; it is also decomposed by milk of lime. With concentrated sulphuric acid, *neriodorin* gives a yellowish-brown colour, which in contact with bromine or nitric acid vapours, changes to violet. Fröhde's reagent gives a violet-red, changing to violet-blue and dirty green. Its neutral aqueous solution gives with ferric chloride a deep reddish-brown colour, and a gelatinous precipitate with basic lead acetate. In presence of sulphuric acid, Nessler's reagent gives a whitish precipitate.

These two bodies, although very closely allied in their properties, may be distinguished by their behaviour with solvents, ferric chloride, basic lead acetate, and Nessler's reagent.

The physiological action and botany of the plant are fully described.

L. T. O'S.

Illicium Religiosum. By J. F. EYKMAN (*Pharm. J. Trans.* [3], 11, 1046—1050).—The fruit (*Star anise*) of this plant, belonging to the family Winteraceæ, is highly poisonous; it is found growing wild in Japan. Its essential oil is highly refractive; of a faint yellow colour, and has the sp. gr. 1.006 at 16.5°; rotatory power, as determined by Hoffmann's polarimeter, is $[\alpha]_D = -8.6$. It does not solidify at -20°. It contains a terpene, b. p. 173—176°, sp. gr. 0.855, and rotatory power -22.5°. A portion of the oil passes over at 231—233°, its rotatory power = 0°, and sp. gr. 1.048 at 12°. Anethol was also detected in the essential oil.

The oil mixes in all proportions with absolute alcohol, chloroform, benzene, glacial acetic acid, carbon bisulphide, and the fixed oils, but is only sparingly soluble in light petroleum and in alcohol of 78.5 per cent. It gives the following reactions:—

Chloral reagent. Colourless, afterwards dirty brown-yellow.

Brom-chloroform (1—20). Colourless, afterwards green-blue, and finally dirty bluish.

Alcoholic hydrochloric acid. Colourless, afterwards blue.

Concentrated sulphuric acid. Dark-red, afterwards purple-red.

Fröhde's reagent. Same as sulphuric acid.

Fuming nitric acid. No action in the cold, orange-red on warming.

Picric acid. Soluble in the cold to yellow-red solution.

Ammoniacal silver nitrate slowly reduced.

Hager's reagent, like sulphuric acid, on addition of alcohol, dark wine-red coloration and reddish-white deposit.

Hydrochloric acid gas. Violet-red, afterwards olive.

1 part of the oil mixed with 6 parts ether-alcohol and treated with 160 grams sodium, gives a greenish-blue, which afterwards passes to yellow. These reactions are compared with *Ol. anisi vulgaris*, *A. stellati* and *fœniculi*.

Seeds.—The seeds yield to light petroleum 30.5 per cent. of a pale yellow oil of sp. gr. 0.919 at 16.5°, soluble in chloroform, ether, benzene, and carbon bisulphide, and sparingly soluble in alcohol and glacial acetic acid. At -20° it assumes the consistency of butter and a white colour. It is a non-drying oil, and, with concentrated sulphuric acid, gives a red-brown colour, and a bright-red with nitric acid containing nitrous fumes; it can be saponified.

From the residue of the seeds freed from oil, the author separates the poisonous principle of the plant by exhausting with alcohol, evaporating the solution, and treating the residue with acetic acid and with chloroform so long as anything is dissolved; the chloroform is then distilled off, the acetic acid evaporated, and the residue treated with water, in which the principle is soluble. The aqueous solution is shaken with light petroleum, treated with potassium carbonate, and shaken with chloroform, which, on evaporation, leaves an amorphous residue; this yields crystalline salts with mineral acids. To this substance, until its identity with some known substance can be established, the author gives the name of "sikimine," from the Japanese name of the fruit "shikimi." It forms prismatic or stellate crystals, sparingly soluble in water, ether, and chloroform, easily in alcohol and glacial acetic acid, insoluble in light petroleum. The impure crystals melt at

175°. When heated, they evolve a peculiar odour, and yield an oily sublimate which does not crystallise from water or chloroform. With Nessler's reagent, the aqueous solution gives a faint turbidity which disappears with excess. Owing to the small quantity of sikimine obtained, its chemical properties could not be further studied. It is highly poisonous, producing cramp of the muscles of the abdomen, tetanus, and vomiting.

L. T. O'S.

Specific Rotatory Power of Parasantonide. By R. NASINI (*Ber.*, 14, 1512—1515).—The specific rotatory power of solutions of parasantonide in chloroform and in acetic anhydride is independent of the concentration of the solution. Experiments made with chloroform solutions between 0° and 40°, show that it is also independent of temperature. On the other hand, the concentration appears to exert a marked influence on alcoholic solutions. With Cornu's polarimeter $[\alpha]_D = +88.43, +89.65$ for solutions in chloroform, and from $+82.08$ to $+83.23$ for solutions in acetic anhydride. For alcoholic solutions, $[\alpha]_D$ varies from $+88.80$ for $\frac{1}{4}$ per cent. solution to $+83.39$ for 8.5 per cent. solution.

W. C. W.

Synthesis of the Quinoline Series. By H. SKRAUP (*Wien. Akad. Ber.* [2], 83, 434—465. A continuation of the author's researches, cf. Abstracts, 1880, 409, &c.).—The author, following out the suggestion of Graebe, that alizarin-blue bears to nitro-alizarin the same relation that quinoline does to benzene, has effected a synthesis of quinoline analogous to that of alizarin-blue. Thus as nitro-alizarin and glycerol give alizarin-blue, $C_{14}H_8(NO_2)_4O_4 + C_3H_5O_3 = C_{17}H_9NO_4 + 3H_2O + O_2$, so nitro-benzene, and glycerol give quinoline: $C_6H_5NO_2 + C_3H_5O_3 = C_9H_7N + 3H_2O + O_2$. But as the liberated oxygen exercises a violent reaction on the products of the change, it is found more practical to use a mixture of nitrobenzene and aniline.

Quinoline.—On treating a mixture of nitrobenzene, aniline, and glycerol in accordance with the equation $2C_6H_7N + C_6H_5NO_2 + 3C_3H_5O_3 = 3C_9H_7N + 11H_2O$ with strong sulphuric acid, a violent reaction occurs at first, which may subsequently be assisted by a gentle heat. The quinoline may be separated from the crude products of the reaction either by saturating with soda and separating the liberated base by distillation in a current of steam, or by treating the residue with ether and then fractionally precipitating with soda.

The author finds that the quinoline synthetically prepared is identical in every respect with the quinoline obtained from cinchonic acid. Quinoline, when oxidised by potassium permanganate, is converted into the *quinolinic acid* of Hoogewerff and v. Dorp (*Abstr.*, 1880, 895). The normal *potassium* salt of this acid forms white needles readily soluble in water, the *potassium hydrogen* salt large rhombic tables, which are completely decomposed at 230° into carbonic and nicotinic acids.

Bases Isomeric with Lepidine.—The author has further studied the similar reaction of the isomeric amido- and nitro-toluenes on glycerol, and has thereby obtained bases isomeric with lepidine, which must be considered to be derived from quinoline by replacement of the

hydrogen-atom in the benzene nucleus. The name *toluquinoline* is proposed for this class of bodies, analogous to Graebe's anthraquinoline (Abstr., 1880, 262) and naphthoquinoline. The reaction whereby these toluquinolines are produced is as follows:— $2\text{C}_7\text{H}_5\text{N} + \text{C}_7\text{H}_7\text{NO}_2 + 3\text{C}_3\text{H}_5\text{O}_3 = 3\text{C}_{10}\text{H}_9\text{N} + 11\text{H}_2\text{O}$.

Orthotoluquinoline is a golden liquid (b. p. 248° , sp. gr. 1.085) easily miscible with alcohol and ether, sparingly with water; it resembles quinoline in its odour, and shows no signs of solidification at the temperature of a freezing mixture. The platinochloride forms dark orange-golden prisms sparingly soluble in water and dilute hydrochloric acid.

The sulphate of hydrogen and toluquinoline forms snow-white prisms sparingly soluble in alcohol, easily soluble in water. The hydrochloride forms transparent prisms, the picrate sulphur-golden leaflets. On heating toluquinoline with methyl iodide, golden crystals of the double compound are obtained, which are immediately decomposed by alkali with formation of a colourless oil. This change is probably analogous to that of quinoline benzyl chloride observed by Claus and Himmelmann (Abstr., this vol., p. 182). *Orthotoluquinoline* is oxidised by alkaline permanganate, with formation of quinolinic acid (*vide supra*).

Paratoluquinoline.—The methylquinoline from 1:4 amido- and nitrotoluene is a golden, refracting liquid (b. p. $257\text{--}258^\circ$, sp. gr. 1.0815); it resembles the corresponding ortho-compound. The platinochloride forms prismatic crystals, the acid sulphate white prisms, the hydrochloride interlaced needles, and the picrate a golden powder. On heating an ethereal solution of the base in a sealed tube with methyl iodide, large golden prisms of the double compound are obtained. Quinolinic acid is also a product of the oxidation of *paratoluquinoline*.

α -Naphthoquinoline is obtained by the action of α -nitronaphthalene and α -naphthylamine on glycerol; it can be separated from the resinous products of the reaction by solution in ether, by subsequent fractional distillation, precipitation of the hydrogen sulphate salt, and finally by separating the base from the salt by ammonia. *Naphthoquinoline* is a colourless oil (b. p. 251° ?), which solidifies after some time into white prisms (m. p. 50°). The platinochloride and hydrogen sulphate form golden prisms, the hydrochloride golden needles, and the picrate microscopic prisms.

The author points out the relations in boiling point of the hydrocarbons and their nitro-, amido-, and quinoline derivatives.

The author considers that these researches offer material support to Körner's hypothesis of the constitution of quinoline. It would appear from the researches of König (Abstr., 1880, 672) that in the first phases of the synthesis of quinoline by the process described above, aniline acrolein is formed, which is subsequently oxidised by the oxygen of the nitrobenzene. This view is supported by the observation that the reaction commences at $150\text{--}160^\circ$, a temperature at which the glycerol sulphate might decompose with formation of acrolein, and further that the distinctive smell of acrolein is noticeable when nitrobenzene and glycerol are heated with sulphuric acid.

V. H. V.

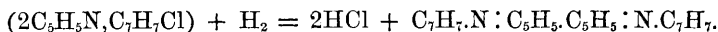
Pyridine Bases. By A. W. HOFMANN (*Ber.*, **14**, 1497—1506).—By the action of silver oxide or potassium hydroxide on methylpyridyl iodide, an oily liquid is formed of strong penetrating odour. The best yield of this substance is obtained by making a mixture of the solid iodide and potassium hydroxide into a thick paste with water. An active reaction ensues, and when this abates the mixture is gently heated until all the water is expelled. The oil contained in the aqueous distillate is collected and dried over potassium hydroxide at 100° , air being carefully excluded. The oil has the composition C_6H_9N . It boils at 129° , and combines readily with oxygen, bromine, iodine, and sulphur. The brown gelatinous hydrochloride gives a dirty yellow amorphous precipitate with platinum chloride.

Analogous compounds are obtained by distilling ethylpyridyl- and amylpyridyl-ammonium iodide with potassium hydroxide. The ethyl derivative boils at 148° , and the amyl derivative at 202° . The amyl derivative dissolves in hydrochloric acid, and is reprecipitated by alkalis. Platinum chloride produces in the hydrochloric acid solution a yellow amorphous precipitate having the composition $2(C_{10}H_{17}N.HCl)PtCl_4$.

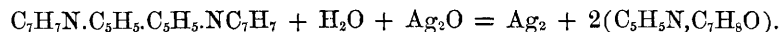
When a cold aqueous solution of methylpyridylammonium iodide is treated with sodium amalgam, a blue coloration is produced, and an oily liquid is formed which slowly solidifies to a crystalline mass. By adding alcohol to its ethereal solution it may be obtained in large colourless crystals which decompose spontaneously. This body precipitates metallic silver from a solution of silver nitrate, a methylpyridyl-ammonium salt being formed.

Similar compounds are produced when ethyl- and amyl-pyridyl-ammonium iodides are treated with sodium-amalgam. They have not however been obtained in the solid state. The compound, $C_{24}H_{24}N_2$, which results from the action of sodium amalgam on benzylpyridyl ammonium chloride is deposited in needles on the addition of alcohol to its ethereal solution.

The formation of this compound may be represented thus:—



The reconversion of this body into the original base by the action of nitrate or oxide of silver takes place according to the following equation:—



The compounds of the alcoholic iodides with picoline and lutidine, when treated with sodium amalgam or alkalis, behave in the same way as their pyridine homologues.

W. C. W.

Constitution of Morphine. By P. CHASTAING (*J. Pharm.* [5], **4**, 19—24).—Morphine, when boiled with alkalis, dissolves in them in equivalent proportions, forming unstable salts which are decomposed by carbonic anhydride, and assume a dark brown colour when exposed to the air, like those of pyrogallol. It would thus appear that morphine is a phenol, which is confirmed by its reaction with ferric chloride.

Potassium morphinate, prepared by boiling morphine with potassium hydroxide and crystallising the solution in a vacuum over sulphuric acid, has the formula: $2C_{17}H_{19}NO_3K_2O + 5H_2O$. The compound, $2C_{17}H_{19}NO_3K_2O + 2H_2O$, has been obtained. It forms a double salt with potassium carbonate, $2(C_{17}H_{18}KNO_3, K_2CO_3) + 2H_2O$.

Barium morphinate, $2C_{17}H_{19}NO_3BaO + 2H_2O$, crystallises more readily than the potassium salt, but is more easily decomposed by carbonic anhydride.

Two *calcium morphinates* have been obtained, $2C_{17}H_{19}NO_3CaO + 4H_2O$ and $2(Ca_{17}H_{18}NO_3)Ca + 2H_2O$.

In the second part of this paper the author shows that since morphine is a tertiary amine and a phenol, there still remains 1 mol. of oxygen, which may or may not be contained in the alcoholic radicals of the tertiary amine. If the oxygen is without the amido-group, then morphine is a tertiary monatomic phenol base combined with CO_2 , which if removed would yield a body bearing the same relation to morphine that phenol does to salicylic acid. Apomorphine also would be morphine deprived of its phenol group, an amide in fact.

By regarding the homologues of morphine as having the above constitution, it is evident that two modifications of the next higher derivative can exist, the CH_2 uniting either with the acid or with the phenolic hydroxyl; in the latter case codeine is the product. The synthesis of codeine by Grimaux supports this hypothesis, the hydrogen of the phenol hydroxyl being replaced by the Me group. The constitution of morphine may therefore be expressed by the formula



The constitution of the group $C_{16}H_{17}$ is still unknown.

L. T. O'S.

New Platinochlorides. By O. HESSE (*Annalen*, **207**, 309—310).—The author has prepared the following platinochlorides of alkaloids by the general method of adding sodio-platinic chloride to a slightly warm solution of the neutral hydrochloride. The salts are nearly insoluble in cold water. The neutral sulphates of conquinine, cinchonidine, and homocinchonidine can be employed instead of the hydrochlorides.

Quinine platinochloride, $(C_{20}H_{24}N_2O_2)_2PtCl_6H_2 + 3H_2O$, is an orange-yellow amorphous precipitate.

Conquinine platinochloride, $(C_{20}H_{24}N_2O_2)_2PtCl_6H_2 + 3H_2O$, forms orange-coloured glittering needles.

Cinchonidine platinochloride, $(C_{20}H_{24}N_2O_2)_2PtCl_6H_2 + 2H_2O$, forms small orange-coloured prisms.

Homocinchonidine platinochloride, $(C_{19}H_{22}N_2O)_2PtCl_6H_2 + 2H_2O$, likewise forms orange-coloured prisms.

J. I. W.

Quinamine. By O. HESSE (*Annalen*, **207**, 288—308).—The author has previously shown that quinamine exists in the barks of *Cinchona succirubra*, *C. officinalis*, *C. Calisaya*, var. *javanica*, and *C. Calisaya*, var. *ledgeriana*. The last-mentioned contains large quantities of the alkaloid. The author finds that the crude mother-liquor of quinine sulphate contains a considerable amount of quinamine. The

substance which he has employed in his researches was derived from this source. 200 kilos. of mother-liquor yield 150 grams of quinamine and 30 grams of conquinamine.

Preparation of Quinamine.—After the alkaloids precipitable by sodium potassium tartrate have been removed, and the cinchonine for the most part separated by precipitating with ammonia and washing the precipitate with ether in which it is scarcely soluble, the ethereal solution is poured into acetic acid. This solution is neutralised, and then, when warm, potassium thiocyanate is added until, on cooling, cinchonine can no longer be detected. Conquinine then comes down, together with a quantity of colouring matter. The clear solution is next treated with sodium hydroxide, and the resinous mass so obtained dissolved in the requisite quantity of 80 per cent. alcohol, from which, on cooling, quinamine is obtained in a crystalline state. After recrystallisation and treatment with animal charcoal, it is obtained quite pure. Its formula is $C_{19}H_{24}N_2O_2$. It is a mono-acid base.

Quinamine hydrochloride, $C_{19}H_{24}N_2O_2HCl + H_2O$, forms hard colourless prisms, which dissolve somewhat easily in cold water, less easily in dilute hydrochloric acid.

Quinamine platinochloride, $(C_{19}H_{24}N_2O_2)_2PtCl_6H_2 + 2H_2O$. The author's recent analyses of this salt agree with those previously made by him (*Annalen*, 199, 336), and he therefore concludes that it contains 2 mols. H_2O . Oudemans, however, found a larger percentage of water.

Quinamine hydrobromide, $C_{19}H_{24}N_2O_2HBr + H_2O$, is prepared by mixing an alcoholic solution of quinamine with hydrobromic acid and evaporating the solution. It crystallises in hard colourless prisms, which are easily soluble in water, and still more so in alcohol.

Neutral quinamine oxalate forms hard colourless needles, which are difficult to separate from an admixed amorphous portion.

Acid quinamine sulphate is obtained as a yellow uncrystallisable residue, which is very soluble in water and alcohol.

Quinamine benzoate, salicylate, and quinate are all obtained by mixing the acids with the base in molecular proportions. None of them have been obtained crystalline.

Action of Acetic Anhydride on Quinamine.—When quinamine is heated at $60-80^\circ$ for several hours with acetic anhydride, 1 mol. of water is given off, and an atom of hydrogen is displaced by acetyl, acetyl apoquinamine being formed.

Action of Ethyl Iodide.—Quinamine dissolves in alcoholic ethyl iodide solution, and on evaporation an amorphous residue is obtained, which dissolves in water on continued boiling. On allowing this solution to cool, quinamine hydriodide crystallises out.

Action of Acids.—Quinamine decomposes readily in an acid solution. The final product, however, varies with the proportions of acid and base employed. I. 1 part of an alcoholic solution of quinamine of sp. gr. 1.125 when heated for three minutes with 20 parts of acid, yields apoquinamine. The solution on continued boiling gives a brown substance, which is extremely insoluble in dilute hydrochloric

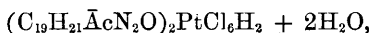
acid. II. If heated with concentrated hydrochloric acid in sealed tubes for some hours at 140° , it is transformed into a caoutchouc-like mass, which is insoluble in all the ordinary solvents. III. If, on the other hand, a mixture of quinamine (1 part) and 13 per cent. hydrochloric acid (10 parts) is allowed to stand for some time, *quinamidine*, mixed with a red oil, separates out. This last alkaloid is also formed when quinamine is heated at 130° in sealed tubes with 1—4 mols. of hydrochloric acid, 1 or 2 mols. of tartaric acid, 2 mols. of quinic acid, or 2 mols. of acetic acid, in the proportion of 1 part of alkaloid to 5 parts of acid. Quinamicine is formed as a bye-product. Quinamidine is also obtained by continued boiling of a solution of quinamine in dilute sulphuric acid (1 part acid to 10 of water), connected with an inverted condenser. Under similar circumstances a mixture of 1 part of acid and 3 parts of water yields apoquinamine.

Apoquinamine, $C_{19}H_{22}N_2O$, as obtained in the preceding manner is purified by dissolving it in acetic acid, boiling with animal charcoal, and reprecipitating with ammonia. The alkaloid crystallises from an alcoholic solution in colourless plates (m. p. 114° uncorr.), which contain no water of crystallisation. Another method of obtaining the substance pure is by heating acetyl-apoquinamine for a few minutes with hydrochloric acid of sp. gr. 1.125. Apoquinamine is thus formed, and on converting it into the neutral oxalate and crystallising from alcohol, it is obtained quite pure. It dissolves in concentrated sulphuric and hydrochloric acids with a greenish-yellow colour, which changes to brownish-yellow on heating. With dilute hydrochloric acid, it yields a colourless solution. From acid solutions, it is precipitated by alkalis in the form of a white powder, at first flocculent, but afterwards crystalline. *Apoquinamine hydrochloride*, $C_{19}H_{22}N_2O \cdot HCl + \frac{1}{2}H_2O$, is obtained crystalline by mixing the base and hydrochloric acid in molecular proportions in alcohol, and allowing the solution gradually to evaporate. The *platinochloride*,



is a yellow powder. The *aurochloride* is a yellow flocculent precipitate. The *hydrobromide* resembles the hydrochloride. The *neutral sulphate*, $(C_{19}H_{22}N_2O)_2SO_4H_2 + 2H_2O$, is obtained in a similar manner to the hydrochloride: it forms thin white needles. The *neutral oxalate*, $(C_{19}H_{22}N_2O)_2C_2O_4H_2 + H_2O$, is prepared like the hydrochloride: it forms short thick prisms. The *nitrate*, $C_{19}H_{22}N_2O \cdot NO_3H$, is obtained in hard granular anhydrous crystals, which are only very slightly soluble in water, but dissolve easily in alcohol. The *tartrate*, $(C_{19}H_{22}N_2O)_2 \cdot C_4H_4O_6 + xH_2O$, crystallises in star-shaped groups of colourless prisms, which dissolve easily in alcohol, but little in cold water. The *quinat*, $C_{19}H_{22}N_2O \cdot C_7H_{12}O_6 + xH_2O$, crystallises in beautiful colourless prisms. The *salicylate* forms an amorphous easily fusible mass. The *perchlorate*, obtained by dissolving the alkaloid in perchloric acid, forms a colourless oil.

Acetyl apoquinamine, $C_{19}H_{21}\bar{A}cN_2O$, is obtained by heating the alkaloid with acetic anhydride. The *platinochloride*,



is an orange-yellow amorphous powder. The *aurochloride* has a similar appearance.

Quinamidine, $C_{19}H_{24}N_2O_2$.—The best method of preparing this body is as follows:—4 grams of quinamine are heated at 130° in a sealed tube with 2 grams of tartaric acid and 18 grams of water for two hours. The tube is then opened, and while the mixture is still warm a saturated solution of sodium chloride is added until it becomes milky. On allowing the mixture to remain at rest, quinamidine hydrochloride separates out, mixed with a certain amount of sodium tartrate. It is purified by precipitating with sodium hydroxide and crystallising from alcohol, when the free base is obtained in small white needles in cauliflower-like clusters (m. p. 93° , uncorr.). It is an isomeride of quinamine, which it resembles in giving a purple-red precipitate with gold chloride; it differs from it, however, in not yielding apoquinamine when treated with concentrated hydrochloric acid. It is a much stronger base than quinamine. It dissolves in concentrated hydrochloric and sulphuric acids with a saffron-yellow colour. The solution in the former acid becomes brown on warming; if it be then poured into cold water it yields a rose-coloured solution with a green fluorescence. The *hydrochloride*, $C_{19}H_{24}N_2O_2 \cdot HCl + H_2O$, crystallises in hard colourless prisms, which are readily soluble in hot water and in alcohol, but insoluble in sodium chloride solution. The salt effloresces in dry air. The *platinochloride*,

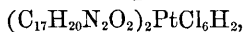


is a pale yellow precipitate, which changes to dark red on standing. The *hydrobromide*, $C_{19}H_{24}N_2O_2 \cdot HBr + H_2O$, crystallises in colourless prisms. The *neutral oxalate*, $(C_{19}H_{24}N_2O_2)_2C_2O_4H_2$, is obtained by mixing alcoholic solutions of the base and acid in molecular proportions.

Quinamicine, $C_{19}H_{24}N_2O_2$.—This body is formed in small quantities, together with quinamidine, when quinamine is heated with acids. It is formed in larger quantities when an alcoholic solution of the base and sulphuric acid is evaporated at 60 – 80° , and the residue so obtained is heated for a few minutes at 100° . A better yield is procured when a drop of glycerol is added to the mixture. The base is freed from admixed quinamidine by repeatedly dissolving it, first in cold water, then in acetic acid, and precipitating with sodium bicarbonate. This treatment is continued until a small quantity of the alkaloid dissolved in hydrochloric acid gives a yellow precipitate with gold chloride, which does not change on standing for some hours. When pure, the crystals melt at 109° (uncorr.). The *hydrochloride* is obtained in a crystalline form by adding a small quantity of hydrochloric acid to a solution of the base in the same acid, and allowing the liquid to evaporate. The *platinochloride*, $(C_{19}H_{24}N_2O_2)_2PtCl_6H_2 + 3H_2O$, is a yellow flocculent precipitate.

Protoquinamicine, $C_{17}H_{20}N_2O_2$.—This substance is obtained by heating the compound composed of equal molecules of quinamicine and sulphuric acid for a short time at 120 – 130° . The mass becomes dark brown, and almost insoluble in water, while the initial substances

were freely soluble. It is purified by dissolving it in acetic acid and precipitating with ammonia. The *platinochloride*,



is a brown flocculent precipitate, which when dried in the air becomes black.

The author gives the following table of the rotatory powers of the preceding alkaloids. p is the weight of substance in 100 c.c. A is the rotatory power $[\alpha]_D$ of the substance dissolved in 97 per cent. alcohol; W , of the substance dissolved in water and known quantities of hydrochloric acid. n is the amount of acid expressed in molecules.

Name of substance.	p .	A .	p .	n .	W .
Quinamine, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$	2	+ 105.5°	2	1	+ 116.0°
Quinamine hydrochloride, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2\cdot\text{HCl} +$	—	—	2	3	+ 117.1
H_2O	2	+ 118.1	2	0	+ 100.0
Quinamine hydrobromide, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2\cdot\text{HBr} +$	—	—	4	0	+ 88.2
H_2O	2	+ 4.5	—	—	—
Quinamidine, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$	—	—	2	0	0
Quinamidine hydrochloride, $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2\cdot\text{HCl} +$	—	—	2	3	+ 47.0
H_2O	2	+ 38.1	2	3	— 28.4
Quinamicine	2	0	2	10	— 29.1
Apoquinamine, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$	—	—	2	3	— 30.0
Acetylapoquinamine, $\text{C}_{19}\text{H}_{21}\text{AcN}_2\text{O}$	2	0	2	10	— 31.2

J. I. W.

Oxidation of Cholic Acid. By M. KUTSCHEROFF (*Ber.*, **14**, 1492—1493).—The author corrects a former statement (*Ber.*, **12**, 1221), regarding the products of the oxidation of barium cholate with sulphuric acid and potassium dichromate. He finds that the chief product is Tappeiner's *cholanic acid* (*Annalen*, **194**, 231), and not cholecamphoric acid.

1 part of cholanic acid requires for solution 3,726 parts of absolute ether, 10,693 parts of water at 20°, and 4,939 at 100°. The solubility of the acid in water increases on prolonged boiling, a fact which may be due to the conversion of cholanic acid into cholecamphoric acid.

W. C. W.

Physiological Chemistry.

Changes of Temperature during Digestion. By R. MALY (*Bied. Centr.*, 1881, 236—237).—When fibrin and coagulated albumen are digested with dilute hydrochloric acid, a considerable lowering of the temperature of the mixture occurs. This is probably due to

heat being rendered latent by the solution of the peptoid bodies formed by decomposition. J. K. C.

Fattening of Pigs with Soja Bean. (*Bied. Centr.*, 1881, 318.)—Three pigs were fed with different quantities of Soja bean, potatoes, and addition of starch, so that the nutrient ratio remained 1 : 4.

Fig.	Nutrients of food given per day, in kilos.	Condition.	Increase in weight per day before fattening, in kilos.	Increase per day during fattening period, in kilos.
I.	{ Proteids 0·573 Fat..... 0·053 Carbohydrate.. 2·163	Very poor in fat.	} 0·14	0·833
II.	{ Proteids 0·571 Fat..... 0·288 Carbohydrate.. 1·581	5½ times fatter than I.	} 0·22	1·06
III.	{ Proteids 0·570 Fat..... 0·303 Carbohydrate.. 1·613	6 times fatter than I.	} 0·16	0·68

In Case I the fat was removed from the beans, and the ratio maintained by large addition of starch. The experiments show the great advantage of feeding with the Soja bean. E. W. P.

Fattening of Pigs with Fleshmeal. (*Bied. Centr.*, 1881, 351.)—Twenty-two pigs were fed for six weeks on potatoes, barley husks, and fleshmeal, to the value of 631 M. The value of the pigs when lean was 1,132 M., and after fattening, 2,112 M., so that there was a gain of 349 M. The proportions employed were 10,000 kilos. potatoes, 1,320 kilos. barley, and 400 kilos. fleshmeal. E. W. P.

Comparison of the Influence of Field Beans and Lupines on the Production of Milk. By O. KELLNER (*Bied. Centr.*, 1881, 311—318).—Lupine seeds have always been found to be harmful to milch cows, and to give the butter and milk an unpleasant taste. The author having devised a method whereby the bitter principle is removed (this vol., 838), has fed cows with seeds so treated, and compared the results with those obtained when beans are used in place of lupines. With lupines a greater yield of milk was obtained, although poorer in dry matter, and also the percentage of butter was lowered. Again, instead of the cows becoming ill, and not thriving, their live weight increased, and neither the butter nor the milk was tainted in any way. To determine whether any harm would ensue by giving a larger quantity of prepared lupines, the ration of these seeds was raised from 2·25 to 3·5 kilos. per day. The cows still increased in weight, and the milk assumed its normal condition as regards dry matter, which had been raised by the use of beans in the first portion of the experiments. The taste of the butter

and milk was not injured. Finally the author concludes that yellow lupine seeds freed by his process from the bitter principle, are the best food that can be given to milch cows.

E. W. P.

Presence of Alcohol in the Animal Tissues. By J. BÉCHAMP (*Bied. Centr.*, 1881, 349).—Traces of alcohol can always be found in the tissues of animals, if it has been administered two hours before death. Hence the discovery of alcohol in the body cannot be considered as sufficient proof of alcoholic poisoning.

E. W. P.

Lactic Acid Fermentation in Urine. By CAZENEUVE (*Bied. Centr.*, 1881, 350).—This form of fermentation is easily produced by adding saccharine matter to urine after it has undergone ammoniacal fermentation. Ammonium lactate is produced at the expense of the ammonium carbonate, and in a few days the urine becomes acid.

E. W. P.

Formation of Hippuric Acid in the Animal Organism. By W. SCHRÖDER, H. WEISKE, and others (*Bied. Centr.*, 1881, 348).—Schröder's results on the elimination of hippuric acid by sheep when fed on potatoes, beans, and benzoic acid, are in opposition to those obtained by Weiske (this Journal, 1877, 217), who found that benzoic acid passed unaltered. Weiske repeated his experiment, and now concurs with Schröder, believing that his former and different results were due to some unexplained abnormal circumstance.

W. Salomon, operating on a rabbit from which the kidneys had been removed, found that after the injection of benzoic acid and glycocine into the stomach, hippuric acid was detected in the muscle, liver, and blood; whereas in the case of carnivora, it exists only in the kidneys. Salkowski shows that phenylacetic acid appears in urine as phenaceturic acid, while phenylpropionic acid is converted into hippuric acid. Stadelmann has studied the conversion of quinic into hippuric acid in the case of dogs and rabbits. Hippuric acid could not be detected in the urine of dogs dosed with quinic acid, but in the case of rabbits fed on milk it appeared after 1—2 days; sodium quinate injected into the jugular vein causes only traces of hippuric acid to appear, as did also calcium quinate when introduced into the stomach.

E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Nature of the Alcoholic Ferment. By D. COCHIN (*Bied. Centr.*, 1881, 346).—It is shown by filtering a fermenting sugar solution through paper and gypsum that no further fermentation takes place in the perfectly clear filtrate, and that therefore the alcoholic ferment is to be considered as insoluble. E. W. P.

Yeast and Fermentation. (*Dingl. polyt. J.*, **240**, 391—401, and 461—466.)—Hayduck has investigated the action of Rochelle salt on

the fermentative power of yeast, and although Meyer states that this salt accelerates the fermentation of a concentrated solution of sugar, Hayduck found it to produce slow fermentation. In concentrated solutions the fermentative power of yeast is decreased, but it does not wholly disappear even in solutions of the highest concentration. With regard to the temperature necessary for the souring of yeast, Delbrück gives 50° , which should be maintained for about 20 hours, and should not be reduced until the acidification is complete. In order to determine the actual yield of yeast in the preparation of the latter, Hayduck mentions that the quantity of water in pressed yeast containing starch varies as much as 10 per cent.; pure pressed yeast yields as a mean 73.5 per cent. of water. To obtain the actual quantity of yeast from the quantity of water contained in yeast contaminated with starch, it is necessary to be in possession of accurate numbers, giving the quantity of water in pressed yeast and moist starch, in the state in which the latter is found in yeast. For pressed yeast 74 per cent. may be taken. Geissler estimates the value of different qualities of yeast as to fermentative power, by adding to 3 to 4 grams of yeast 100 c.c. of a 10 per cent. solution of sugar. The mixture is kept at a temperature of 25° to 30° for an hour, and the quantity of carbonic anhydride evolved is determined. Besides gypsum, starch forms the chief adulterant of yeast. The quantity of starch is determined by its conversion into sugar. It has been proposed to separate starch from yeast by elutriation, the former depositing more readily than the latter. According to Hayduck, the variable fermentative power of yeast depends mainly on the quantity of starch contained in pressed yeast, but also on the different constitution of the yeast cells, and the percentage of protein substances present. The durability of yeast is influenced in two ways. Certain qualities can be pressed only with great difficulty; they remain soft, and do not assume the normal consistency characterising pressed yeast. Others assume their normal consistency at first, but afterwards become soft and give off an offensive odour, a circumstance due to the formation of bacteria in the malt or rye used in mashing. It is therefore recommended to increase the degree of acid fermentation and the temperature in the mash. For the preparation of yeast, Werner and Krüger give a temperature of 60° to 61° . According to Stumpfheldt, all substances which form a gelatinous mass at a temperature not higher than that at which the protein substances are coagulated, can be used for preparing yeast. In the preparation of pressed yeast, the largest yield is obtained when the formation of yeast is completed in the first operation, called the "main fermentation," as here the strongest evolution of carbonic anhydride takes place. Märcker has investigated the influence of various substances on fermentation. There is an increase of yeast when acetic acid is absent; when present in yeast to the extent of 0.6 per cent. the growth of the latter ceases. The same is the case with butyric acid. Lactic acid, however, increases the yield. Rainer prepares pressed yeast without vinous fermentation, by extracting the albuminous substances from cereals, maize, leguminosæ, bran, &c., with 15 to 20 times the quantity of slightly alkaline water, and peptonising with about 4 per cent. lactic acid, or 0.25 per cent. phos-

phoric acid, or 0.4 per cent. sulphuric or hydrochloric acid at 38° or 40°, or by macerating these substances with the above acids in weak solutions, and converting into peptones with the addition of 1 part dried malt for 1 part by weight of dry albuminous substances.

D. B.

Behaviour of Fungi in the Animal System. By P. GRAWITZ (*Bied. Centr.*, 1881, 319—321).—These interesting observations are a counterpart of those made by Buchner, who succeeded in transforming hay bacteria into those which produce splenic fever. In a former communication, Grawitz showed that some affections of the skin and mucous membrane could be produced by fungi, which seemed identical with *Mycoderma vini* and *Oidium lactis*, but which had been cultivated. Further experiments have been made. *Pencillium* and *Eurotium glaucum* have been cultivated first on bread, then in slightly acid solution of peptone containing 1 per cent. of sugar, then reducing the acidity, and finally in an alkaline solution of peptone. No difference in appearance is observable, but when introduced into animals, these altered fungi cause speedy death.

E. W. P.

Influence of Intermittent Light on the Formation of Chlorophyll. By WIESNER (*Bied. Centr.*, 1881, 352).—It is considered that the formation of chlorophyll by the action of light is a photochemical inductive process, because the exposure for $2\frac{1}{2}$ minutes of etiolated barley and oat seedlings to continuous light did not result in the formation of chlorophyll, but when after a dark interval light was again allowed to act, then chlorophyll was produced; so that the effect of the light was to induce the formation only, as at the end of a single period of illumination no more chlorophyll was observable than at the beginning, again with continuous illumination the first trace of chlorophyll was only observable after five minutes. Long continued illumination, and illumination in excess will, however, give rise to the production of this substance.

E. W. P.

Influence of Light on the Growth of Beet. By H. BRIEM (*Bied. Centr.*, 1881, 280).—Beetroot grown under trees was found to run much more to seed, and ripen less early, than plants grown in the open. The relation of weight of leaves and roots was in the shade, 66 : 34; in the open, 35 : 66. 1,000 plants in the open yielded 32.5 kilos. sugar, while the same number grown in the shade produced only 13.4 kilos.

J. K. C.

Influence of Light on the Ripening of Grapes. By A. LEVY (*Annales Agronomiques*, 6, 100—111).—In order to study the influence of light on the ripening of grapes, certain clusters were enclosed, directly after flowering, in an apparatus which kept them in complete darkness, whilst it allowed a free circulation of air, and maintained the same temperature and degree of humidity as in the case of adjacent clusters on the same stem, allowed to mature in sunlight under ordinary conditions. Full details of the construction of the apparatus and of the thermometric, hygrometric, and actinometric observations during the process of ripening, are given in the paper. The grapes

ripened in darkness were healthy, plump, and covered with bloom, but rather paler in tint than those exposed to the light. The peduncles of the former clusters were, however, much more lignified than those of the ordinary clusters, which were green and tender at the time of harvest. During the whole time of ripening, the grapes exposed to light contained more sugar and less acids than those in the dark. The mean result of analyses executed from September 2nd to September 26th, is as follows:—

	Sugar per cent.	Acids per 1,000.
Grapes exposed to light.....	19·83	7·39
" " darkness ..	16·28	8·91

J. M. H. M.

Influence of Atmospheric Electricity on the Growth of Grapes. By J. MACCAGNO (*Bied. Centr.*, 1881, 332).—Copper wires 80 cm. long terminating in platinum points were attached perpendicularly to 16 vines; wires also connected the stems of the vines with the ground. The product of these vines compared with that of 16 other neighbouring plants, shows a difference which the author considers is due to electricity. The vines to which the wires were attached yielded a greater quantity of must and sugar, and less acid.

E. W. P.

Cultivation of Hops. By MÜNTZ (*Bied. Centr.*, 1881, 331).—Analyses of various parts of the hop plant show that, generally speaking, the daily assimilative energy is greatest during the last part of the plant's life, but in the first period of the plant's growth, a greater amount of nitrogen, potash, and phosphoric acid is assimilated than during the latter part.

Animal droppings are the best manure for hops, minerals being unnecessary, as so little ash is contained in that portion removed from the land.

E. W. P.

Evolution of Carbonic Anhydride by Plant Roots. By CAUVET (*Bied. Centr.*, 1881, 279).—The plants were placed in flasks containing distilled water, and kept constantly in the dark; air freed from carbonic anhydride was kept constantly bubbling through, and the evolved CO₂ was weighed. The mean results were as follows: Evolved carbonic anhydride from 6 a.m. to 10 a.m., 0·03546 gram; from 10 a.m. to 2 p.m., 0·03368 gram; from 2 p.m. to 6 p.m., 0·03413 gram. It appears, therefore, that the evolution is considerable, and greater in the day than at night.

J. K. C.

Germination of Fir Seeds. By F. NOBEE (*Bied. Centr.*, 1881, 278).—Those seeds which are in the middle of the cone retain their vitality the longest; the beginning of October is recommended as the best time for collecting the cones to be used for seed.

J. K. C.

Analysis of Lichen Esculentus (Manna). By E. LATOUR (*Bied. Centr.*, 1881, 353).

In Parts per 100 of Manna.

Water.....	7.00	Sand.....	12.00
Fat and wax	0.73	SiO ₂	traces
Chlorophyll	0.27	Fe ₂ O ₃	3.120
Mucilage	3.30	CuO.....	12.256
Sugar { Crystallised....	1.20	Na ₂ O.....	0.040
{ Non-crystallised	2.87	CO ₂	9.460
Lichenin.....	10.75	SO ₃	0.144
Nitrogenous matter	1.89	HCl	0.048
Cellulose and lignose ..	31.99	P ₂ O ₅	2.768
	<hr/>	Loss	0.164
	60.00		<hr/>
			40.000
			E. W. P.

Report on the Experimental Plots at Grignon in 1879. By P. P. DÉHÉRAIN (*Ann. Agronomiques*, 6, 71—99).—This paper contains an account of the cultivation of potatoes, maize, oats, and sainfoin, in the experimental plots at Grignon in the year 1879. The results obtained by the use of different manures are detailed and tabulated. J. M. H. M.

Experiments with Potatoes. By F. JACOBS and others (*Bied. Centr.*, 1881, 251—262).—This is an account of the crops obtained by various experimenters from different kinds of potato: amongst those sorts recommended for quality and quantity of yield may be mentioned Champion, Richter's Emperor, Eos, &c. J. K. C.

Specific Gravity of Potatoes. By H. FRESSENIUS (*Anal. Zeitschr.*, 20, 243—248).—The sp. gr. of potatoes stands within narrow limits in fixed relation to the percentage of starch in the tubers. It is usually determined either by Balling-Fresca's method (weighing in air and in water) or by that of Fresenius-Schulze (floating in sodium chloride solution and taking sp. gr. of solution in the ordinary manner). It having been alleged that the two methods gave discordant results, the author has determined the sp. gr. of 25 different kinds of potatoes by both methods. The results agreed closely in all cases.

The sp. gr. varies considerably with different tubers even of the same kind, but bears no relation to the size of the potato.

O. H.

Chunnos Potatoes from Peru. By MEISE (*Bied. Centr.*, 1881, 281).—The dried substance of these potatoes contained 94 per cent. starch, as against 84.8 in ordinary potatoes (mean of seventy analyses); 2.6 per cent. of protein, instead of 7.4 in ordinary tubers; 0.4 ash, as against 4 per cent.; and 1.31 per cent. of matter soluble in water (sugar, dextrin, &c.), as against 18 per cent. J. K. C.

Preservation of Diffusion Residues from Beet-Sugar Manufacture. By M. MÄCKER (*Bied. Centr.*, 1880, 237—239).—These residues on keeping for several months lose from 30 to 50 per cent. of their solid constituents, probably by fermentation. To obviate this, a

drying apparatus has been patented by Blossfeld to dry the residues, after which they do not suffer so much loss. J. K. C.

Nutritive Value of Diffusion Pulp and of Pulp from the Hydraulic Press. Determination of Nitrogen in the Different States in which it exists in Vegetable Products. By H. PELLET and C. LE LAVANDIER (*Ann. Agronomiques*, 6, 111—126).—The extraction of sugar from beet by diffusion into water, instead of by the old process of submitting the grated roots to hydraulic pressure, is very general in Austria and Germany, and has been gaining ground in France. The authors' experiments were undertaken to determine the relative feeding value of the pulps yielded by the two processes.

Four samples were analysed: (A) Pulp from hydraulic press, two years old; (B) ditto, new; (D) diffusion pulp, two years old; (E) diffusion pulp, new. Percentage of dry matter, corrected for sand and earth: A, 20·08; B, 22·45; D, 12·88; E, 12·24. With respect to the dry matter, therefore, 167 parts diffusion pulp are equivalent to 100 parts pulp from hydraulic press. Nitrogen per cent. of dry matter: A, 1·045; B, 1·160; D, 1·366; E, 1·190. From this point of view, 152 parts diffusion pulp are equivalent to 100 parts hydraulic press pulp. The mechanical condition of the diffusion pulp is, however, more favourable to digestion than that of the press pulp.

In order to make the comparison closer, the authors have determined the proportion of nitrogen in the four different states: (1) ammoniacal nitrogen; (2) as nitric acid and nitrates; (3) alkaloïdal nitrogen (glutamine, asparagine, betaine), and (4) albuminoid nitrogen. The total nitrogen is made up, in 100 parts, of—

	A.	B.	D.	E.
Ammoniacal nitrogen	3·45	7·09	1·68	0·17
Nitric „	1·97	1·78	—	—
Alkaloïdal „	54·24	36·59	14·72	25·87
Albuminoid „	40·34	54·54	83·60	73·96

Taking into consideration albuminoid nitrogen only, there is little difference between the average of the two pulps.

In the second part of this paper, the authors describe in detail the methods employed by them for the estimation of the four types of nitrogen mentioned above.

Ammoniacal nitrogen is estimated by distilling 5 grams of substance with pure magnesia (adding 1 gram paraffin to prevent frothing) for 15 minutes, and titrating the distillate with standard soda.

Nitric nitrogen is determined by a modification of Pelouze's process, which has been described in *Bull. Soc. Chim.* for October 5th, 1876. By this process a few milligrams of N_2O_5 may be easily estimated.

Alkaloïdal Nitrogen is obtained by difference, the total nitrogen being estimated by a combustion with soda lime.

Albuminoid Nitrogen.—Five grams of dry matter are treated with 100 c.c. boiling water, and $\frac{1}{4}$ c.c. of acetic acid; the liquid is boiled for 15 minutes. By this means the albuminoids proper and the soluble albuminoids are coagulated. The whole is made up to 100 c.c. with boiling distilled water and allowed to settle, the liquid decanted, and

filtered through two tared filters. By this treatment the nitrates, ammonia salts, asparagine, betaine, tyrosine, leucine, and all soluble matters are dissolved. The albuminoid nitrogen is then determined by a combustion of the dried precipitate with soda lime.

J. M. H. M.

Prevention of Lupine Sickness. By J. KÜHN (*Bied. Centr.*, 1881, 240—245).—The author has shown that lupine sickness is not caused by the alkaloids which are always present in lupines, but by a substance which only occurs under certain conditions in the plant. This body he has termed ictrogen: it can be destroyed by four hours' steaming under two atmospheres' pressure, as well as by washing with cold water. The washings will produce the sickness if mixed with the diet of sheep. Steaming alone does not effectually destroy ictrogen, except when under pressure. Kellner's method of first steaming and then washing with cold water, produces a fodder which is perfectly harmless and easily digestible: mere drying of the lupines does not remove any of their injurious qualities. The author recommends testing the lupines however prepared, before giving them as fodder for cattle.

J. K. C.

Temperature of the Soil under Snow. By E. and H. BECQUEREL (*Bied. Centr.*, 1881, 289).—Experiments conducted during the winter 1879–80, on the temperature of bare soil and soil covered with turf, showed that the temperature fell considerably in the first case, and not perceptibly below 0° in the latter; when snow covered the bare soil, the temperature still sank below 0°, from which it is concluded that turf, or any close growing plant, is a warmer covering to the soil than snow.

E. W. P.

Influence of Superficial Drying on the Temperature and Moisture of the Soil. By E. WOLLNY (*Bied. Centr.*, 1880, 223—226).—A thin layer of dry soil or sand was found to diminish considerably the loss of water by surface evaporation from the soil, and the same effect was produced by hoeing or harrowing the surface after some time; the temperature of the soil was also increased by the presence of a thin layer of dry soil at the top, but diminished by hoeing or covering the surface with sand.

J. K. C.

The Form of Combination in which Phosphoric Acid Exists in the Soil. By P. P. DÉHÉRAIN and KAYSER (*Bied. Centr.*, 1881, 290).—Some soils are not rendered more productive by manuring with superphosphates. This occurs only when the phosphoric acid is present in the state of calcium phosphate soluble in ammonium citrate and acetic acid.

A soil may have a considerable amount of phosphates present, and yet be unfertile, for the reason that the phosphates are those of aluminium and iron. When soil contains more than 0.4 per cent. = 1,500 kilos. per hectare of phosphates, addition of phosphates as manure is unnecessary; naturally the figure must be raised if iron and aluminium phosphates are present.

E. W. P.

New Method of Ascertaining the Absorptive Power of a Soil. By R. ZALOMANOFF (*Bied. Centr.*, 1881, 226—228).—The old method, agitation of the soil with the solution in a flask, is open to some objections, such as the possible formation of precipitated phosphates, evolution of carbonic anhydride, &c. By simply allowing the solution to filter gently through the soil, these disadvantages are obviated, the results obtained differ, however, considerably from those given by the old method. Experiments were tried with loam, crushed marble, and powdered granite. J. K. C.

Mechanical and Chemical Analyses of Roumanian Soil. By S. P. RADIU (*Bied. Centr.*, 1881, 293).—The soils which belong to the quarternary period are of three kinds: black (*Pamentul negru*), grey, and yellow diluvium; the first covers the plains of Roumania to a depth of 1—3 meters, the yield of grain being on the average 22 bushels per acre, and never less than $16\frac{1}{2}$: this, as the land is not highly cultivated, must be due in great measure to the large amount of organic matter present. The grey diluvium covers the plateaux, and is not so fertile, being more clayey. The yellow soil is found on the hill sides to a depth of 13—20 meters, and consists of fine sand, mica, and felspar, contains lime and a considerable amount of potash, and is capable of bearing grapes. The firmness of the soils is shown by mechanical analysis to be due to the very fine sand, and not to a large amount of clay, the maximum of the former material being 55 per cent., and of the latter 11·5—both in the grey soil. The maximum percentage of the principal constituents are as follow:— Fe_2O_3 , 1·3; CaO , 1·2; MgO , 0·16 in the yellow soil; K_2O , 0·25; P_2O_5 , 0·14; N , 0·23 in the black; and Al_2O_3 , 4·35, in the grey. E. W. P.

Manuring Experiments on "Donaumoos." By F. SCHAFFERT (*Bied. Centr.*, 1881, 302—306).—Donaumoos is a district consisting of a dry moor 17,000 hectares in extent, the soil of which is 3 metres deep, resting on a retentive clay, and contains but little plant food; the analyses show 3·36 per cent. of nitrogen, 84·2 of organic matter, 0·029 K_2O , 0·246 P_2O_5 . By reason of bad farming, the crops are reduced to a minimum, succeeding best in a wet season, for, during dry weather, the soil becomes excessively dry, and is readily blown away. Stable manure, kainite, superphosphate, and Lahn phosphorite were used as manures on the experimental plots, on which were sown summer rye and potatoes, and with the following general results:—Rye after potatoes is better than potatoes after rye; gain is experienced by allowing the manures to act for three crops, and more so with superphosphate than with phosphorite. Experiments on meadow land show that only Peruvian guano and bone-meal are of any value; other manures are applied only at a loss. E. W. P.

Manuring Experiments at Lutter. (*Bied. Centr.*, 1881, 233—236.)—The results of work in the year 1880 are given in a tabular form, from which it is seen that of the potatoes, Zborower yielded the best net results. Stable manure produced with several kinds the largest gross yield, but the least net profit. The largest crop of beet

was obtained from the small Wanzlebener, manured with Chili saltpetre, guano, and superphosphate.

J. K. C.

Experiments with Sewage. By H. MARIÉ-DAVY (*Bied. Centr.*, 1881, 231—233).—These researches were carried on in large cases made of cement; the soil consisted in some cases of poor sand, and in others of good heavy soil from the banks of the Seine. The experiments were carried on with grasses, barley, beetroot, rape, &c. The grasses and corn gave tolerably good yields, but the linseed and hemp did not thrive well.

J. K. C.

Manuring Experiments on Fruit Trees. By P. SORAUER (*Bied. Centr.*, 1881, 307—310).—As want of food exerts a harmful influence on fruit trees, so does an excess of manure; in the latter case the foliage becomes dark-green and remains weak, and the root tips become swollen. Two kinds of cherry-tree plants, the sweet and agriot cherry, were submitted to water culture in large and small vessels; the strength of the solutions was one half-thousandth and one half-hundredth; the results were that in the more concentrated solutions the leaf surface and dry matter produced were less than when the solutions were more dilute; so that in spite of the greater quantity of food, the plants remained smaller than when the food was in smaller quantity; but the percentage of dry matter shows that the plant was more solidly constructed. The first plant, grown in $\frac{1}{2}$ per cent. solution, was richer in dry matter, as well as in ash. Comparing those plants grown in large and in small vessels, the agriot yielded a larger amount of leaf and dry substance when grown in small vessels, whereas with the sweet cherry the reverse was the case. When grown in dilute solutions the agriot caused the evaporation through its leaves of twice as much water, and the sweet cherry under the same conditions of a third more water, than when the solutions were more concentrated. The absolute evaporation per gram dry matter increases until the wood is ripe, and then continues at a constant rate.

E. W. P.

Garden Manuring Experiments. By W. LAUCHE and A. ORTH (*Bied. Centr.*, 1881, 228—231).—These researches extended over three years; the crops raised were chiefly cabbages and swedes. For 100 kilos. of stable manure were added, in various cases, 240 grams ammonium sulphate, 285 grams potassium sulphate, 285 grams Chili saltpetre, and 593 grams superphosphate: without stable manure double these quantities were used: besides these, 2.5 kilos. of lime and 8 cans of night soil. The highest yields were never obtained by the use of stable dung alone; in the first two years quicklime and clay marl, and in the wet year, 1880, a mixture of ammonium and potassium sulphates with superphosphate proved the best additional manure. Where the mineral manures are given alone, care must be taken that they are not too strong, and are used in the right proportions: their exclusive use is, however, not to be recommended. Chili saltpetre gave better results, in 1880, than ammonium sulphate, especially when given alone. Of greater importance, however, is the

remarkable increase in the effect of the artificial manures when applied in solution. In 1878 a mixture of ammonium and potassium sulphates, with superphosphate in the dissolved condition, produced a crop of carrots half as large again as when given in the dry state. In 1880 only half the quantity of dissolved mixture was given compared to the dry, but the yield of swedes was more than twice as great. The addition of lime or wood-ashes to stable manure and night soil produced a better result in every case.

In the after effect, stable dung, with quicklime and clay marl, proved superior to all the other manures. Next in order comes stable dung and quicklime, then the former with potassium sulphate. Even in this case, liquid manures gave better results than dry.

J. K. C.

Testing the Progress of Putrefaction in Manure Heaps. By MEDICUS (*Bied. Centr.*, 1881, 275).—A sample is taken from the centre of the heap by means of a forked stick; if it appears homogeneous, tolerably moist and warm and with no abnormal smell, the manure is supposed to be ready for use. Should the sample be hot, very dry, and have a strong ammoniacal odour, the process of putrefaction has gone on too quickly, and must be stayed by cold water or putrefied liquor. If the sample is cold, and pieces of straw are visible, putrefaction is aided by pouring blood on the heaps.

J. K. C.

Researches on the Changes Occurring in Stable Manure when Kept. By BIRNER and BRIMMER (*Bied. Centr.*, 1881, 298—300).—To determine the changes which occur when dung is kept moist, dry, or mixed with chalk, gypsum, kainite, sulphate of magnesia, lime, or peat, equal volumes of horse and cow dung were placed with 1—2 per cent. of the above-mentioned substances (peat was used to the amount of 10 per cent.) in large glass vessels, and kept for half a year sheltered from rain and sun. A table of loss in nitrogen, water, &c., is given, and from it is gathered that the loss of nitrogen which is occasioned by rotting is inconsiderable only when the manure is sheltered from wet and air, but occurs to a large extent if the dung be kept wet; 1 per cent. chalk, $\frac{1}{2}$ per cent. lime, and 5 per cent. peat caused the greatest loss. Gypsum prevents loss. Kainite and magnesium sulphate seem to induce an absorption of nitrogen from the air, as does also the addition of $2\frac{1}{2}$ per cent. of lime and 10 per cent. of peat powder.

E. W. P.

Wool Waste as Manure. (*Bied. Centr.*, 1881, 275).—Thirty samples of wool waste were analysed at the experiment station of Dahme. On the average they contained 3.91 per cent. nitrogen, but varied from 1 to 6 per cent.

J. K. C.

Preparation of a Manure from Molasses Waste. (*Bied Centr.*, 1881, 276).—The waste is mixed with a solution of salt and powdered charcoal, and dried. Bone meal which has been decomposed with sulphuric acid is next mixed with it, and the whole dried and powdered.

J. K. C.

Manuring Wheat, Barley, and Oats with Saltpetre. By H. CHANCELLOR (*Bied. Centr.*, 1881, 300—302).—The results of the experiments made in the wet season of 1879 show that the best yield of grain is obtained when the saltpetre is added in quantities of about 1 cwt. per acre at intervals of 2—3 weeks. The wheat straw was much increased, and also the weight of grain; with barley the increase was very marked. The quality of the oats was good, although the yield was but medium.

The author considers that saltpetre acts best in dry seasons.

E. W. P.

Cultivation and Manuring of Leguminosæ. By E. WEIN (*Bied. Centr.*, 1881, 329—331).—Yellow, brown, round black, and long black Soja beans have closely approximating compositions, but the round black is the lowest in albumen and the long black in fat. Compared with peas, hog beans, and field beans, the Soja bean gives the best yield, and flourishes best when there are 20 plants per square metre. As manure, Chili saltpetre is the best suited for yield and albumen.

E. W. P.

Manuring of Sugar Beet. By CHAMPONNOIS and PELLET (*Bied. Centr.*, 1881, 297).—The manure was dug in 2 cm. deep, and the seeds before sowing were soaked for four days in liquid manure, then sown so that the plants should be 0.1 m. apart on the ridges, which were distant 0.8 m. from one another. The plots measured 19 sq. m. The manures, pure mineral, and mineral with much organic matter, consisted of 3 parts Chili saltpetre, 5 parts superphosphate, 3 parts potassium chloride, and 2 parts ammonium sulphate. The organic manure obtained from molasses waste (*melasseschlempe*) contained nearly the same amount of mineral ingredients; but in addition organic matter equal to about three times the quantity of potash, and these mixtures were applied at the rate of about 340 lbs. per acre. Various kinds of beet were sown, and it was found that in all cases the yield was highest in those plots manured with the "organic" mixture; and that although the percentage of sugar per root was rather lowered, yet the absolute quantity was increased; the amount of ash is practically unaltered, and as the cost was 216 M. lower per hectare than the mineral manure, this organic mixture is highly to be recommended.

E. W. P.

Analytical Chemistry.

Differential Method of Specific Gravity Determination.

By W. DITTMAR (*Chem. News*, **44**, 51).—To determine the difference in specific gravity between two liquids, the author uses the following apparatus:—

(1.) A cylindrical specific gravity bottle provided with a perforated glass stopper and a hook for suspending it from the balance by a fine platinum wire.

(2.) A cylinder large enough to float the bottle, supposing it to be suspended in a mass of liquid within the cylinder.

(3.) A balance so arranged that things can be suspended below the pans, and when thus suspended are at a convenient working height.

After having ascertained (once for all) the capacity of the bottle for water, charge it with liquid I, suspend it from the balance within a mass of the same liquid, and ascertain its apparent weight (p' grams); then repeat the experiment with liquid II *inside*, and note down the result, p'' . If the capacity of the bottle is $= v$ fluid grams, we obviously have $v(s'' - s') = p'' - p'$, or—

$$s'' - s' = \frac{p'' - p'}{v}.$$

In both weighings care must be taken to give the inner liquid time to assume the temperature of the outer. As will be easily seen, one of the advantages of this method is that the result is relatively independent of errors in temperature.

D. B.

New Apparatus for use in Gas Analysis. By J. A. WANKLYN and W. J. COOPER (*Phil. Mag.* [5], **11**, 534—536).—The authors fit to the flask used in Pettenkofer's method for estimating carbonic anhydride, a hollow flask-like stopper of thick glass, the neck of which is ground into the neck of the glass bottle. Into this flask the baryta-water is placed, and the stopper is then inserted. By this arrangement when it is necessary to estimate carbonic anhydride in a gas lighter than air, no loss is incurred by the necessity of opening the bottle to add the baryta-water. By replacing the baryta-water by lead acetate or standard acid, sulphuretted hydrogen or ammonia may be estimated.

L. T. O'S.

Note on Incineration. By J. LÖWE (*Zeits. Anal. Chem.*, **20**, 223—225).—Currents of air favourable to rapid incineration are produced by putting the platinum crucible in a circular hole in a slightly curved clay dish about 12 cm. in diameter, which is placed slightly slanting upon an ordinary tripod over a Bunsen burner.

O. H.

Analyses of Furnace Gases. By H. BUNTE (*Zeits. Anal. Chem.*, **20**, 163—178).—A reply to critical observations made by A. Wagner (*ibid.*, **19**, 434) as to the trustworthiness of the analyses made at the Munich "Heizversuchstation." The author shows that the methods in use at that place are the most trustworthy at present available, and that the limits of probable error involved are comparatively small.

O. H.

Estimation of Phosphorus in Slag from Blast Furnaces. By C. MÜLLER (*Dingl. polyt. J.*, **240**, 384).—The author states that most chemists fail to detect the presence of phosphorus in basic slag from blast furnaces. As the slag is a product of a reducing fusion process, it may be supposed that the phosphorus, like the sulphur contained in it, is not combined with oxygen, but with a metal, probably calcium, and that by treating the slag with hydrochloric acid as usual,

phosphoretted hydrogen is formed by the decomposition of the phosphide, besides sulphuretted hydrogen, both escaping without detection. The author uses an apparatus for estimating the amount of phosphoric acid in slag, which has been devised by Ledebur for the determination of sulphur in pig iron. The slag is dissolved in concentrated hydrochloric acid, and the gases evolved are oxidised with fuming nitric acid. The sulphuretted hydrogen evolved forms sulphuric acid, and the phosphoretted hydrogen phosphoric acid. After the evolution of gas has ceased, carbonic anhydride is passed through the apparatus. The phosphoric acid is then determined in the usual manner. D. B.

Nessler's Test for Ammonia. By T. SALZER (*Zeits. Anal. Chem.*, 20, 225—231).—It is proposed to utilise this reagent for the detection of free or so-called half-combined carbonic acid in water, and of caustic alkalis in presence of carbonate. O. H.

Estimation of Reduced or Precipitated Phosphates. By A. HERZFELD and G. FEUERLEIN (*Zeits. Anal. Chem.*, 20, 191—208).—It is shown that from concentrated solutions of CaHPO_4 in ammonium citrate, ammonia precipitates CaNH_4PO_4 , which salt always enters in larger or smaller proportion into the ammonium-magnesium phosphate precipitate, and causes the amount of phosphoric acid to appear higher than it really is. Hence the magnesium precipitate must necessarily be redissolved in acid and reprecipitated, or the phosphoric acid contained in it determined by uranium solution.

According to the authors, the solubility of calcium phosphate in ammonium citrate does not appear to be due to double decomposition, but to the formation of a double salt (not specified in the original paper).

The ammonium citrate solution is advantageously prepared by mixing 300 grams of citric acid with 325 grams ammonium carbonate, dissolving the mixture in water, and diluting the solution until it has a sp. gr. of 1.105 (to about $1\frac{1}{2}$ litres). O. H.

Determination of Sulphur. (*Dingl. polyt. J.*, 241, 51—55).—In the estimation of sulphur by combustion in oxygen, Mixer passes the vapours escaping from the bromine solution, treated with an excess of bromine and a small quantity of hydrochloric acid, through a tube inserted in the bottom of a bottle of 8 litres capacity, in order to condense the vapours therein. At the end of the operation the bottle is washed out with water, and the liquid added to the bromine solution. Zulkowsky also recommends combustion of the sulphur in oxygen, but absorbs the vapours in a solution of potassium hydroxide and potassium hypobromite. The latter is obtained by dissolving 180 grams potassium hydroxide (purified with alcohol) in water and gradually adding 100 grams bromine, the operation being conducted in the cold. The liquid is diluted to 1 litre, 30 c.c. being sufficient to determine 0.5 gram sulphur in a sample.

According to Gröger, the sulphides of iron contained in iron pyrites are converted into iron monosulphides when heated with metallic iron covered with a layer of calcium carbonate. By adding dilute

hydrochloric acid to the mass, sulphuretted hydrogen is evolved, which is passed through a solution of iodine, and determined in the usual manner.

Drown proposes to heat finely-divided sulphides with sodium hydroxide solution of 1.25 sp. gr. He gradually adds an excess of bromine to the mixture, and finally acidifies with hydrochloric acid. The solution is evaporated to dryness, taken up with acidified water and precipitated with barium chloride. D. B.

Estimation of Potassium as Platinochloride. By ZUCKSCHWERT and WEST (*Zeits. Anal. Chem.*, **20**, 185—191).—In a circular sent to the German potash manufacturers in May, 1880, Tatlock strongly recommended the use of a method of his own for the determination of potash. The authors have, at the request of the Stassfurt manufacturers, very carefully tested Tatlock's method, and compared it with that recommended by Fresenius (*Quantit. Anal.*, 6th Edit.). They find that the results obtained by Tatlock's method are invariably about 0.35 per cent. *too low*.

Fresenius' method has been somewhat simplified at Stassfurt, without materially influencing the accuracy of the results, and is there carried out as follows: 10 grams of the well-mixed sample are dissolved in 500 c.c. water, and 20 c.c. of this solution are mixed in a basin with 7 c.c. of platinum chloride solution, containing 10 grams platinum in 100 c.c. The contents of the basin are evaporated on the water-bath to a syrupy consistence, and, after cooling, the solid mass is mixed with 10 c.c. of strong (95 per cent.) alcohol, the solution filtered through a weighed filter, and the washing with alcohol repeated two or three times. The residue of platinochloride is dried for about half an hour at 110—115° C. As a rule not more than 50 c.c. alcohol is used. O. H.

Solubility of Cadmium Sulphide in Ammonium Sulphide. By H. FRESenius (*Zeits. Anal.*, **20**, 236—242).—A. Ditte has stated (*Compt. rend.*, **85**, 402) that, contrary to generally accepted statements, cadmium sulphide is soluble to a very considerable extent in hot or cold ammonium sulphide, the hot solution as it cools depositing transparent crystals of CdS, whilst not less than 2 grams of the sulphide remain dissolved in 1 litre of ammonium sulphide.

The author has carefully tested Ditte's statements, and finds that they are greatly exaggerated. He precipitated solutions of cadmium sulphate, and also digested pure freshly precipitated cadmium sulphide, with various amounts of colourless ammonium sulphide, of ammonium sulphhydrate, and of yellow ammonium sulphide, and found the solubility of CdS in 1,000 c.c. of each reagent at 60° to be as follows:—

In (NH ₄)HS	0.0706 gram
„ (NH ₄) ₂ S	0.0677 „
„ (NH ₄) ₂ S ₂	0.0773 „

Thus, whilst cadmium sulphide is slightly soluble in the agents employed, its solubility is too small to be of moment, even in quantitative.

tive analyses with the small amounts of the sulphide solutions usually employed. O. H.

Fehling's Solution. By C. ARNOLD (*Zeits. Anal.*, **20**, 231—233).—Volhard's method of copper titration (*Zeits. Anal.*, **18**, 285) is recommended for the standardising of Fehling's solution. O. H.

Determination of Chromium in Chrome Iron Ore. By H. N. MORSE and W. C. DAY (*Chem. News*, **44**, 43).—From 6 to 10 grams potassium hydroxide are placed in a wrought-iron crucible (capacity 100 c.c.), and gently heated until the fused mass becomes tranquil. After cooling, the finely-pulverised material, weighing not more than 0.5 gram, is placed on the potassium hydroxide and evenly distributed over the surface. A flame just sufficient to thoroughly fuse the alkali is applied to the uncovered crucible, and the contents, as long as they remain in a fluid condition, are frequently stirred with a piece of iron wire, which is allowed to remain in the crucible. Within two hours' fusion the decomposition is complete, and the bottom of the crucible becomes dry. The latter is then turned on its side, and the temperature raised to a dull red heat. At the end of two or three hours the mass becomes rapidly yellow, owing to the oxidation of chromium to chromate. Portions of the mass retain a greenish colour, however long the heating is continued; but this is due to the presence of iron and manganese, and not to unoxidised chromium. The mass, after cooling, is dissolved in hot water, filtered to remove iron, and the filtrate rendered slightly acid with nitric acid. The aluminium is precipitated with ammonia and washed by decantation. The potassium chromate is then reduced, and the silica rendered insoluble by evaporating to perfect dryness, with an excess of hydrochloric acid. The residue is moistened with hydrochloric acid, taken up with water, and filtered. The chromium in the filtrate is separated from magnesium and determined as chromic oxide. D. B.

Wood Spirit for making Methylated Spirit. By C. BARDY (*J. Pharm.* [5], **4**, 24—31).—The author reviews the legislation with regard to the preparation of methylated spirit, and the methods for the analysis of wood spirit. He proposes a method for its analysis involving the principles of those of Krömer (*Ber.*, **13**, 1000) and Güming, and it can be applied to the original wood spirit or the methylated alcohol. The method is not described in this part of the paper, which is to be continued. L. T. O'S.

Comparative Experiments on the Behaviour of Thymol and Phenol with Different Reagents. By E. HIRSCHSOHN (*Pharm. J. Trans.* [3], **12**, 21—22).—*Millon's Reagent*.—Thymol (1—1000) gives turbidity; on boiling, the solution becomes clear with violet-red coloration, and turbid again on cooling. 1 in 16,000 gives a pale coloration, the smallest quantity that can be detected.

Phenol gives a red coloration, more or less intense, according to the state of dilution. According to Almén 1 in 2,000,000 can be detected.

Calcium Hypochlorite and Ammonia.—*Thymol*.—5 c.c. of a solution of

thymol (1—1000) are rendered turbid and opaque by 4 drops ammonia and 1 drop of bleaching powder solution; on boiling, flocks separate, and the solution assumes a greenish colour. In more dilute solutions (1—4000) turbidity alone is produced; 1 in 32,000 becomes turbid only on boiling. The green colour imparted to phenol cannot be detected in solutions more dilute than 1—400 (Almén 1—5000).

Sodium hypochlorite gives with thymol a turbidity which in solutions 1—1000 remains in presence of excess of the reagent, but solutions containing 1—16,000 and less become clear when excess is added. With phenol, however, a turbidity is formed which is not permanent until a certain quantity of reagent has been added, and even then if it is treated with a still further quantity of the reagent, a point is reached at which the turbidity again disappears.

Chlorine-water may be used to distinguish between thymol and phenol in the same manner as the previous reagent, similar results being obtained. In the case of thymol, on adding ammonia to the turbid mixture, a solution, more or less greenish, is produced. Chlorine-water may be used to detect the presence of thymol in phenol, by avoiding excess of the reagent, a decided turbidity being produced.

Bromine-water gives with thymol a similar reaction to that with phenol, but it is more sensitive, 1 in 60,000 giving a decided turbidity.

Gold chloride is reduced by thymol, the solution becoming greenish-black; 1 in 50,000 produces this result in 15 minutes. It is only after a lapse of some time that phenol produces a similar reaction.

Platinum chloride, like gold chloride, is reduced by thymol, but only on boiling, when the solution becomes cloudy, opaque, or transparent according to the dilution. Solutions of phenol remain clear on boiling.

Nitric acid.—When boiled with nitric acid, solutions of thymol are coloured from golden- to pale-yellow according to dilution, and generally become opaque or opalescent; a solution containing 1—4000 remains clear.

Solutions of phenol are all coloured more or less yellow, and become clear by boiling, except solutions diluted to 1 in 1000.

L. T. O'S.

Determination of Starch in Pressed Yeast. By M. HAYDUCK (*Bied. Centr.*, 1881, 343).—It having been found by several analyses of pressed yeast free from starch, that the amount of water present is 74 per cent., it is possible, by the use of the following formula (of which the previous steps are fully detailed) to estimate the amount of starch in other than pure pressed yeast:—

$$x = 2.63b - 9.47,$$

where x = the pure yeast, and b = the amount of water in 10 grams of the impure material.

E. W. P.

Estimation of Carbonic Anhydride. By T. S. GLADDING (*Chem. News*, 44, 4).—The apparatus used consists of the ordinary generating flask, followed by an empty U-tube, to retain condensed water-vapour; this is succeeded by four potash-bulbs of the Geissler

form: the first of these contains sulphuric acid to dry the gas; the next two contain potash solution of sp. gr. 1.27 for absorbing the carbonic anhydride; the last contains concentrated sulphuric acid, to absorb the moisture taken up from the potash solution. Then comes the U-tube, containing soda-lime and serving as a guard. The last three Geissler bulbs constitute the weighable portion of the apparatus. Perfectly dry air and carbonic acid enter these, and perfectly dry air alone escapes. The advantages of this apparatus are, that concentrated sulphuric acid is superior to calcium chloride as a drying agent on account of its greater avidity for moisture, its non-absorption of carbonic anhydride, and its greater cleanliness and simplicity of renewal. The rapidity with which an analysis may be made, and the fact that large quantities of substance may be used with corresponding increase of accuracy, is also an advantage. D. B.

Lactic Acid in, and Alcoholic Fermentation of Milk. By G. Musso (*Bied. Centr.*, 1881, 344—346).—In only three out of eight samples of milk examined was any free acid detected, and as it was volatile in the vapour of water, it could not be, according to the author, lactic, but must be acetic acid. Titration with soda-solution for the estimation of free lactic acid (see this Journal, 1879, 749) is of no value. The amount of lactic acid necessary to produce curdling of milk varies with the temperature and the percentage of casein. Concerning the fermentation of milk-sugar, the author says that there is no constant relation between the amount of sugar decomposed, and the carbonic anhydride and lactic acid produced, between temp. 28—40°; for every 100 sugar there may be produced 3.27—28.21 CO₂. The nearer the temperature approaches that of a room (15°), so much the more acid will be formed; alcohol and saccharomyces are produced. Milk from various sources does not ferment with equal readiness. E. W. P.

Estimation of Salicylic Acid in Beverages. By A. RÉMONT (*J. Pharm.* [5], 4, 34—35).—200 c.c. of cider or beer, freed from carbonic acid by heating to 58—60°, or of wine reduced to one-third its volume by distillation at 70—80°, are treated three times with an equal volume of ether, and the ethereal solution decanted and distilled. The residue is washed with ether into a tared flask and weighed. It is then treated three times with a volume of chloroform sufficient to dissolve the whole mass if it were salicylic acid (1 c.c. dissolves 0.022 gram). This solution is made up to 100 c.c., and the salicylic acid determined by comparing the coloration produced by ferric chloride in 5 c.c. of solution with that produced in 5 c.c. of a solution containing 0.2 gram acid per litre, which must be freshly prepared whenever required for use. L. T. O'S.

Rapid Estimation of Uric Acid. By A. PETIT (*J. Pharm.* [5], 3, 533—534).—200 c.c. of urine are strongly agitated with 5 c.c. of fuming hydrochloric acid for five minutes, and allowed to stand for one hour. The uric acid which separates out is then collected on a weighed double filter-paper, dried at 100°, and weighed. To avoid

error from the presence of silica in the precipitate, it is ignited, and the residue, if any, subtracted from the total weight. L. T. O'S.

Estimation of Morphine in Opium. By E. MYLIUS (*Pharm. J. Trans.* [3], 12, 6—9).—This is a colorimetric method based on Neubauer's process (*Zeits. Anal. Chem.*, 2, 331), of removing the iodine liberated from iodic acid by morphine, by carbon bisulphide. The author compares the colour of the solution with that produced by a standard morphine solution, since he finds that within certain limits the quantity of iodine liberated is proportional to the quantity of morphine present. Contrary to Stein (*Arch. Pharm.*, 198, 150), the author finds that the colour is not affected by pure acetic acid or by alcohol or hydrochloric acid in small quantities, but in large quantities the last body prevents the coloration completely. Sugar, nitric, phosphoric, and sulphuric acids do not prevent the coloration, but gum and tannin prevent the separation of the carbon bisulphide and its coloration. A large quantity of an acetate prevents the coloration by combining with the iodic acid.

The method of procedure is as follows:—0.5 gram powdered opium is boiled with 10 c.c. water, 3 grams basic lead acetate are added, the whole made up to 50 c.c. with cold water, and after shaking, the solution is filtered. To the filtrate, or a given portion of it, 15 drops of sulphuric acid are added and filtered. This filtrate is used for the determinations.

The standard morphine solution is prepared by dissolving 0.1 gram morphine in 100 c.c. water, and adding 3 grams of sulphuric acid. The two tubes used for holding the solutions are graduated to 20 c.c. in $\frac{1}{5}$ c.c. Into each tube a drop of a concentrated iodic acid solution (or 0.08—0.1 gram potassium iodate and 2 drops sulphuric acid) is introduced, then 5 c.c. of rectified carbon bisulphide, and finally 10 c.c. of the standard morphine solution into one tube, and into the other 10 c.c. of the extract. The tubes are then briskly shaken for two to four minutes, and then allowed to rest for 10 minutes, until the carbon bisulphide separates, when the tints of the two columns are compared. If they differ in tint, more carbon bisulphide is added to the darker solution until the tints are alike; then if y = the amount of CS_2 , and x the percentage of morphine in the opium, we have (I) $5 : 5 + y = 10 : x$ (Ia) $5 + y : 5 : 10 : x$, according as the standard solution contains less or more morphine than the opium. Again, morphine may be added to the fainter solution until its colour is equal to the other, when we have the equations—

$$(II.) \quad 10 : 10 + y = 10 : x \text{ and } (IIa) \quad 10 + y : 10 = 10 : x.$$

This method, although not as exact, is more expeditious than Flückiger's, which requires 24 hours and 4 grams of substance, whereas 20 minutes and 0.2 gram suffice in this case. L. T. O'S.

Adulteration of Olive Oil. By M. CONROY (*Pharm. J. Trans.* [3], 11, 933—934).—After detailing the various methods suggested for detecting cotton-seed oil in olive oil, the author describes a modification of Pontet's process.

Nine parts of oil are mixed with 1 part nitric acid, sp. gr. 1.42, and heated until action sets in; the source of heat is then removed, and the mixture, after being stirred until the action ceases, is left to cool, when olive oil sets to a pale straw-coloured mass in about two hours; whilst cotton-seed oil assumes a deep orange-red colour. By comparing the colour of a suspected oil when thus treated with that of pure olive oil, adulteration to the extent of 5 per cent. may readily be detected. This test may be rendered quantitative by comparison with samples containing known quantities of cotton-seed oil. L. T. O'S.

Examination of Milk. (*Dingl. polyt. J.*, **241**, 50).—Heeven uses an apparatus called a "pioscope," consisting of a disc of caoutchouc, with a flat elevation in the centre 2 cm. in diameter and a ridge 0.33 mm. high. By pouring a few drops of milk on the raised surface and placing a flat glass over it, a layer of milk 0.33 mm. thick is obtained, which partly or wholly conceals the black disc of caoutchouc. In accordance with the quantity of fat present in the milk, more or less dark bluish-grey colours are obtained. Six of these shades are printed on the ridge of the glass cover, with marks corresponding with the quantity of fat present in the milk. The colours represent the following qualities:—Cream, very fat, normal, little fat, poor, and very poor. D. B.

Tannic Acid as Alkalimetric Indicator. By W. BACHMEYER (*Zeits. Anal. Chem.*, **20**, 234).—The well-known production of a brown-red coloration in tannic acid solutions by caustic alkalis, especially ammonia, is proposed to be utilised in alkalimetric titration. It is stated that 1 part of alkali in a million parts of water still distinctly furnishes a coloration. O. H.

Valuation of Hops. By C. O. CECHE (*Zeits. Anal. Chem.*, **20**, 180—184).—The author in very general terms, and without giving any analyses, proposes to determine the lupulin, tannic acid, resinous matters, and chlorophyll, and expresses a hope that the quality of hops may be estimated from these determinations as a basis. O. H.

Valuation of Barley. By V. GRIESMAYER (*Bied. Centr.*, 1881, 287).—The barley is cleared in the weighed sample from dead seeds and all foreign matter by soaking in water; it is then boiled, and the amount of starch determined by conversion into sugar. As the correct result, the mean of five determinations is taken. J. K. C.

Bornträger's Aloes Test. By R. H. GROVES (*Pharm. J. Trans.* [3], **11**, 1045).—This test, described in the *Zeits. Anal. Chem.*, **20**, 234, depends on the red colour imparted to ammonia by benzene, after shaking with the substance containing aloes. The following precautions to be observed are detailed by the author:—

In the case of Natal aloes, the test cannot be applied in solution containing less than 1 per cent., and in no case in solutions containing 1 in 250.

The colour is not due to aloin, and, if due to tannin, the variety is soluble in benzene.

In substances containing tannin, care must be taken that the benzene solution is perfectly clear before it is decanted, otherwise the suspended tannin will give a coloration with ammonia.

L. T. O'S.

Testing Peru Balsam. By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], 12, 45—47).—The author reviews at length the different methods for determining the value of Peru balsam, and draws special attention to the following conclusions:—

The sp. gr. of Peru balsam at 15° must be between 1·140 and 1·145. Experience may extend the limits from 1·138 to 1·146. The numbers 1·15—1·16, as generally given, are much too high.

Ten drops of balsam with 0·4 gram of slaked lime produce a soft mass; but if adulterated, the mass becomes very hard. If castor oil is present, this is not effectual, but the addition of the lime renders the odour of the oil perceptible, especially if warmed.

Shaken with three times its weight of carbon bisulphide, the cinnamoin (benzyl cinnamate) is dissolved, imparting but little colour to the solvent, whilst the insoluble dark-brown resin attaches itself firmly to the glass.

L. T. O'S.

Estimation of Peptones. By DEFRESNE (*Pharm. J. Trans.* [3], 12, 8—9).—The author points out the errors to which the usual methods are liable, and advises that, first a qualitative analysis of the peptone be made.

The presence of gelatin is shown by saturating the peptone with hot magnesium sulphate, when the gelatin separates. In this case, the value of the peptone is determined by estimating the total nitrogen, and also that in the gelatin, and multiplying the difference of the results by 6·05, which will give the weight of dry and pure peptone.

If gelatin is absent but glucose present, which is shown by the iodine reaction, the peptone is estimated by the determination of the nitrogen.

If neither of the above are present, 10 grams of pepsin are shaken with 100 grams absolute alcohol, and then 50 grams ether are added; after standing three hours, the precipitate is collected, dried at 100°, and weighed. By calculating the weight found in 100 grams solution and adding 5, the weight of dry peptone is obtained.

To separate glycerol, if present, the solution is evaporated at 90°, until the weight is constant. The residue is treated with a mixture of alcohol and ether (4 : 1), which dissolves the glycerol only.

L. T. O'S.

Technical Chemistry.

Colliery Explosions. By F. A. ABEL (*Chem. News*, **44**, 16—18, 27—31, and 39—42).—The principal facts, which are more or less conclusively demonstrated by the results obtained in the experiments with dust from Seaham Colliery and other sources, forming the subject of this very extensive paper, are summarised as follows:—

1. Several of the samples of dust collected in Seaham Colliery last November exhibited signs of having been affected by heat. The two samples taken from the floor and off timbers at the curve in the stone drift (in proximity to where the shot was fired at the time of the explosion), as also the sample from near Maudlin engine, exhibited no signs of having been affected by heat.

2. The samples of Seaham dust exhibited considerable differences in regard to richness in coal, fineness and uniformity in this respect, density, &c.; the proportion of coal ranged from about 96 to below 54 per cent. in the dry sifted samples. The chemical and microscopical examination did not furnish any data to lead to conclusions as to the extent to which the dust may have taken part in the production or augmentation and transmission of the explosion at Seaham Colliery; but there was evidence of the existence of partially burnt dust at a number of points very distant from each other and in different directions in the colliery.

3. The several samples of dust differed from each other considerably in sensitiveness, the most sensitive of the Seaham dusts were found to be those which were the richest in coal, and also those which contained the highest proportions of very fine dust.

4. Comparing the samples of Seaham dust with dusts obtained from other collieries where disastrous explosions have recently occurred, it was found that the most sensitive of the former was somewhat less sensitive than samples of dust obtained from Leycett Colliery (Fair Lady Pit), which ranked highest in this respect among all the samples experimented with. The Leycett dusts correspond closely in chemical character and sp. gr. with the purest Seaham coal-dust; their somewhat greater sensitiveness is probably due to their remaining more uniformly suspended in air currents, but possibly also to physical peculiarities.

5. One of the Seaham dusts, which ranked high (third) in order of sensitiveness, contained the lowest proportion of coal of all the samples, and consisted of non-combustible matter to the extent of nearly half its weight. Special experiments were made in consequence of this behaviour, showing that some perfectly non-combustible powders, not susceptible of any chemical change when exposed to the action of flame, are very little inferior to the most inflammable or sensitive of the Seaham dust samples in their power to bring about ignition of an otherwise unflammable mixture of fire-damp and air.

6. Mixtures of fire-damp and air in proportions bordering on those which will ignite on the approach of flame, are inflamed instantaneously.

neously if they contain in suspension only a few particles of such non-combustible dusts, or of the Seaham or other dusts from coal pits.

7. This effect appears ascribable in part to the fact that these dust particles, when they pass through a lamp flame, immediately become incandescent, and thereby localise and intensify the heat at those points, and thus bring about the ignition of the mixture of air and fire-damp by which they are surrounded.

8. The smallest proportion of fire-damp experimented with (from the nine-foot Wigan mine) which became ignited and produced explosive effects, when passing a naked lamp at a velocity of 600 feet per minute, having suspended in it the most sensitive of the Seaham dusts, was 2.5 per cent., and with the most sensitive Leycett dust, 2 per cent.

9. In a current moving at a velocity of only 100 feet per minute, the Leycett coal-dust, suspended in air containing only 1.5 per cent. of fire-damp became ignited by the lamp flame, the ignition extending throughout the mixture. The accidental presence of a small proportion of fire-damp, caused one of the most inflammable of the coal-dusts (from Leycett) to become inflamed and to carry fire some distance, when a small powder charge was fired from a cannon while the dust was travelling.

10. The sensitiveness to ignition of a mixture of air with a small proportion of fire-damp is considerably increased if the source of heat is increased.

11. The results of the experiments with Seaham and other dusts appear to show (*a*) that coal-dust in mines not only much promotes and extends explosions, but (*b*) that it may also be itself readily brought into operation as a fiercely-burning agent which will carry flame rapidly as far as its mixture with air extends, and will operate even as an exploding agent; (*c*) that dust in coal mines, quite apart from any inflammability which it may possess, can operate in a distinct manner, as a finely divided solid, in determining the ignition of mixtures of only small proportions of fire-damp and air, and consequently in developing explosive effects; (*d*) that a particular dust in a mine may therefore be a source of danger, even though it contains only a small proportion of coal or combustible matter.

12. The proportion of fire-damp required to bring dust in a mine into operation as a rapidly burning or exploding agent is below the smallest amount that can be detected in the air of a mine, even by the most experienced observer with the means at present in use.

13. In the complete absence of fire-damp, coal-dust exhibits some tendency to become inflamed when passing a very large lamp flame at a high velocity; but so far as can be determined by experiments on a moderate scale, this tendency is of a limited nature, and very different from the property of carrying or propagating flame, which even comparatively non-sensitive dusts possess in the presence of a very small quantity of fire-damp.

In conclusion, it is mentioned that it can scarcely be maintained that the air of a mine in which the coal gives off gas at all can be, at any time, free from fire-damp, and as the existence of very small quantities of that gas in the air of a mine suffice to bring about the

ready propagation of flame by coal dust, it would appear needless to assume that coal-dust, in the entire absence of fire-damp, may give rise to explosions even of only limited character in coal mines, in order to account for casualties which cannot be ascribed to the existence of accumulations or sudden outbursts of fire-damp. D. B.

Influence of Coal-Dust in Colliery Explosions. By W. GALLOWAY (*Chem. News*, **44**, 16).—Referring to the three great colliery explosions of the past year, namely, Risca, Seaham, and Penycraig, the author mentions that whatever may be the results of experiments with coal-dust made on a small scale, this is not a mere question of "adding fuel to the flame," of "aggravating the consequence of an explosion," of "spreading an explosion," or of "lengthening out the flame of fire-damp," or that of a blown-out shot. Given a well-ventilated or badly-ventilated dry mine, with moderately clean fine dry coal-dust lying everywhere all over the workings, and of any quality, then if an explosion be begun at any point in one of the only three possible ways—(1) by the coal-dust being raised and ignited by a blown-out or other shot; (2) by an explosive accumulation of fire-damp and air being ignited by a blown-out or other shot; (3) by an explosive accumulation being ignited accidentally by a defective or other safety-lamp, or in any other manner—and if it accumulate a certain degree of fuel without dying out, that force will go on increasing, and the explosion will inevitably extend to every open space in the workings, whatever may be their extent or ramifications. Fire-damp plays a most important part in every great explosion. D. B.

Preparation of Phosphates. By E. and H. ALBERT (*Bied. Centr.*, 1881, 276).—The authors recommend mixing the phosphate for half an hour with the sulphuric acid. By this means it is easily ground, and loss of phosphoric acid from imperfect decomposition avoided. J. K. C.

Manganese in Steel. By S. KERN (*Chem. News*, **43**, 266).—Many works using inferior materials for the production of cast-steel, add a notable quantity of spiegeleisen or ferro-manganese: hence steel cast in such works often contains 0.60 to 1.0 per cent. of manganese. Such steel is good for many purposes, but in some cases (for boiler making and ship-building) it requires serious consideration whether it is advisable to use such a material, the liability to corrosion of which is very great and the bending tests unsatisfactory. The author believes that inspectors, before passing plates for the above-mentioned purposes, should be acquainted with the chemical composition of the steel. Thus much confusion may be avoided. D. B.

Elimination of Carbon Bisulphide from Commercial Benzene by Alcoholic Potash. By B. NICKELS (*Chem. News*, **43**, 250).—The author treats 100 c.c. of the sample of "benzole" and "toluole" with 1 gram of potassium hydroxide previously dissolved in the smallest quantity of boiling absolute alcohol. Potassium xanthate separates, which is filtered off and the fluid portion washed with its

own volume of slightly warm water by brisk agitation in a glass, separating funnel closed with a stopper. After separating the alcohol, the liquid (benzole or toluole) is treated with gypsum in a dry bottle to dehydrate it, and then submitted to examination. This operation is repeated until deposits of xanthate are no longer obtained.

D. B.

Souring of Yeast. By M. DELBRÜCK (*Bied. Centr.*, 1881, 273—274).—The souring of yeast is generally allowed to take place between 40° and 50°. The author found that at 40° butyric acid was formed, which acts as a strong poison for yeast; care must therefore be taken that a temperature of 50°, which favours the production of lactic acid, is maintained during the whole of the souring process.

J. K. C.

Action of Cold on Ropy Wine. (*Bied. Centr.*, 1881, 342).—Wine that remained thick and ropy, not yielding to any treatment, was exposed to hard frost; the wine then became clear, the impurities being retained by the ice formed.

E. W. P.

Influence of Temperature on the Composition and Amount of Extract obtained from Malt. (*Bied. Centr.*, 1881, 357).—The amount of extract obtained from malt increases up to a certain point with the time that the malt remains on the malting floor. Piling it up decreases the yield of extract. The amount of nitrogen diminishes with the amount of heating; slow malting at low temperatures causes a larger amount of nitrogen to appear in the extract. The change in the amount of nitrogen produced by malting at high temperatures, does not correspond with a change in the diastatic action of the malt.

E. W. P.

Influence of Oxygen on the Clarifying of Beer. By H. HOLZBECKER (*Bied. Centr.*, 1881, 357).—A short technical paper in which a method is described of clarifying thick beer by aërating it

E. W. P.

Method of Preserving Brewers' Grains. By SALOMON and M. HERTER (*Bied. Centr.*, 1881, 350).—The grains are baked into a loaf, which may be softened with water, or broken up for the use of the animals.

Herter proposes to mix the grains in a pit with straw chaff in layers. Grains so mixed will keep for a long period.

E. W. P.

Sugar Manufacture. (*Dingl. polyt. J.*, 241, 40—48).—*Purification of Beetroot-juice.*—At the Gaudersheim sugar refinery the juice is treated in the "first saturation" with 1·8 per cent. lime calculated on the original beetroot, and carbonic anhydride introduced until the juice shows 0·15 per cent. of alkalinity. The mass is passed through filter presses, and the clear liquid treated in the "second saturation" with 0·18 per cent. lime, and carbonic anhydride again introduced until 0·08 per cent. alkalinity has been obtained. The mass is again filter-pressed and the clear juice treated in the "third saturation" with sulphurous acid. The alkalinity is reduced to 0·03 per cent.,

and the whole thrown on filters, filled with gravel. The thin juice obtained is evaporated, refiltered, and finally boiled down in vacuum pans. At the Ouzie sugar works an inferior beetroot is worked up. The juice is treated with more lime at a temperature of 69°, and the whole heated to 85°. The carbonic anhydride is pumped into a receiver, whence it is introduced into the saturation vessel. Thus it is possible, in spite of more lime being used, to complete the saturation in a short time, as a uniform stream of carbonic anhydride at any desired pressure can be obtained. The clear portion of the juice is treated with phosphoric acid which removes part of the calcium salts without materially altering the alkalinity. The mass is then filtered. A sample of the diffusion-juice showed 7·8 saccharometer, 6·1 polarisation, and 7·8 quotient. The addition of phosphoric acid has, however, the advantage of separating arabin, a substance having a considerable influence on the formation of molasses.

In the remaining portion of the paper, practical data are given as to the appearances observed in the saturation process. It is shown that, in order to obtain good results, the saturation should be completed in as short a space of time as possible.

D B.

Use of Parchment-paper in Osmose. By A. ECKSTEIN (*Dingl. polyt. J.*, 241, 48).—About four years ago, Dubrunfaut introduced a method of osmosing sugar molasses on a large scale, and recommended the use of Belgian parchment-paper for diaphragm. The author having had a large experience in the manufacture of parchment-paper, found that the ordinarily prepared paper was insufficient for dialysing purposes. The same was the case with endless paper. As the thickness of ordinary paper is irregular, parchment-paper prepared from it shows thick, thin, firm, and loose places: hence the passage of liquid through it will be irregular. By doubling or trebling parchment-paper these difficulties are overcome. The sheets of paper are laid above one another, and intimately united.

D. B.

Ziemann's Process for the Manufacture of Butter and Cheese. By A. BERGMANN (*Bied. Centr.*, 10, 118—121).—According to this method, cream or skimmed milk is allowed to stand until too thick to pass through a linen filter; the liquid is then filtered through linen, and the solid left behind is gently pressed for some hours. In the case of cream, the solid is washed with water and converted into butter in one of Ziemann's machines; where skimmed milk has been used, the solid mass left behind, after pressing, is already a kind of soft cheese. The following numbers compare the yield obtained by this method with the ordinary process:—

	From 100 kilos. cream.	From 100 kilos. milk.
Ziemann's method..	22·5 kilos. butter	11·67 kilos. cheese
Ordinary ,, ..	17·75 ,,	9·50 ,,

This method, however, is not to be recommended for the preparation of butter, because there is very little time or labour saved, and also because the yield of fat is no greater, a larger quantity of butter

being obtained only at the expense of its quality and value. On the other hand, with regard to the preparation of cheese, it may be considered as very advantageous, both the quality and quantity being improved. J. K. C.

Milk, Butter, and Cheese. (*Dingl. polyt. J.*, **240**, 224—227.)—Mitzinger's milk-cooler consists of two horizontal tubes, fitted concentrically into one another, the space forming the ring being provided with notched sheet-iron, which is said to divide the milk more finely.

Klebs preserves milk by evaporating it at a temperature of 40° to 50° in a vacuum apparatus to one-fifth of its volume. During the evaporation 1 to 3 litres of a solution of 50 grams benzoate of magnesium in 1 litre of water are added for every 100 litres of milk.

Fleischman describes a series of experiments made with Laval's separator, the yield of cream being larger than that obtained by the ice method.

Arnim mentions that "skimming processes" which do not yield sweet milk fit for the human palate are of little value at the present time.

Herter shows that the "blueing" of milk is not due to disease of cows, but depends on the amount of moisture present in the warm air in the place where the milk is stored.

With regard to the spreading of disease by means of milk, Airy found that by boiling the latter it is rendered innocuous.

The action of rennet on milk has been studied by Mayer, who found that a temperature of 39° was the most suitable for coagulation: the question, which has been often raised, as to whether during the coagulation heat is absorbed or given up was also investigated, the results showing that up to the commencement of the coagulation, a regular decrease of 0.04° to 0.06° in temperature is occasioned per minute.

In America, butter is adulterated with powdered talc, prepared in Cincinnati. To colour butter, oleomargarin, and cheese, annatto, the colouring matter of *Bixa orellana*, is used. D. B.

Peculiar Property of Gutta-percha. (*Dingl. polyt. J.*, **240**, 363.)—It is known that gutta-percha is rendered plastic when placed into water at 60 — 70° : hence it is used for the production of fine impressions; it is, however, less well known that soft gutta-percha is elastic and resists blows with a hammer. When thrown against a solid wall its form remains unaltered, whilst it is considerably affected when subjected to moderate pressure. This peculiar property is attributed to the presence of occluded air in the plastic substance.

D. B.

Sewage in Oysters. By C. A. CAMERON (*Chem. News*, **44**, 52).—Large numbers of oysters, collected by dredges off the coast of the county of Wexford, are laid down in "beds" on the northern shore of the Bay of Dublin. Owing to the recent construction of many large sewers, the contents of which are discharged into the northern side of Dublin Bay, the Clontarf oysters are not thriving well, and great numbers of them die shortly after their translation from their native

habitat. Some oysters were examined taken from a place where the tides cover them to a height of about ten feet, and which, during low water, is nearly dry. In most of the oysters the brine was without any peculiar odour, but in a rather larger proportion there was a very slight, but distinctly foetid odour, whilst in a few cases there was a strong and unmistakable odour of sewage. Examined microscopically, the liquid in the oysters which had a foetid odour was found to swarm with micrococci and other low organisms similar to those usually present in sewage. Chemical analysis confirmed the microscopic examination. It is thought that the illness which so many persons have experienced after swallowing oysters believed to have been stale, was really due to the presence of sewage in the juice of the molluscs.

D. B.

Wilkinson's Process for the Manufacture of Gas from Wood.

By C. A. DOREMUS (*Chem. News*, **44**, 31—33).—The essential feature of the process consists in reducing the carbonic anhydride to carbonic oxide, and at the same time getting rid of all tar, acids, and waste products. This is accomplished by forcing the gas through a bed of red-hot charcoal. After the first charge of wood has been carbonised, the charcoal, instead of being drawn, as with coke, is pushed back into the retort. The gas made from the second charge is therefore obliged to pass through this layer of red-hot charcoal to reach the stand-pipe at the rear of the "through" retort. The heat is pushed to get as large a yield of gas as possible, and the reduction of carbonic anhydride correspondingly facilitated. The water in the wood is also an active agent, since in this superheated state it forms water-gas with the aid of the charcoal. The gas needs but slight purification. Nitrogen in the form of ammonia is virtually absent; little sulphur exists in any form, neither sulphuretted hydrogen nor carbon bisulphide being found, except in traces, whilst there is no trace of tar. To prevent too great an accumulation of charcoal, the retorts are drawn twice a day. 53,832 cubic feet of gas are produced from a cord of wood, costing 5.25 dols. per cord of 3,300 lbs. The quantity of gas alone is thus four times as great as that which can be obtained from coal, costing an equal sum per ton as does wood per cord.

It is still customary with the gas works in New York to manufacture a poor quality of coal-gas, which is, along with the wood-gas, afterwards carburetted, and in which form it is called "commercial" gas, and has a great candle power. The yield of coal-gas is 14,645 cubic feet per ton of coal, costing 5 dols. From this sum the price received for coke, tar, and gas liquor must be deducted. Prior to admixture with naphtha-vapour, the coal and wood-gases are purified and passed to the storage-holder. From this the gas enters an illuminator, so constructed that the naphtha running in is converted into vapour by steam-heat, and thoroughly mixed with the gas. From the illuminator the mixture of gas and vapour passes into superheated retorts to be "fixed." 4.5 gallons of naphtha are used for every thousand feet of commercial gas. 100 volumes of the commercial gas of the New York Mutual Gas Company consist at present of 21 volumes of wood-gas, 37.4 volumes of coal-gas, and 41.6 volumes of naphtha gas.

D. B.

General and Physical Chemistry.

Measurement of the Actinism of the Sun's Rays, and of Daylight. By R. A. SMITH (*Proc. Roy. Soc.*, **30**, 355—359).—The method employed depends upon the fact that when potassium iodide in solution is treated with nitric acid in so small a quantity as to cause no change of colour in dull diffused daylight, a change takes place when the same mixture is brought into clear light, iodine being set free and the solution becoming yellow; the liberated iodine may then be titrated with thiosulphate. The paper gives examples of the application of the process, which, however, do not admit of abstraction.
H. W.

Widening of the Hydrogen Lines. By C. FIEVEZ (*Compt. rend.*, **92**, 521).—The widening of the hydrogen lines when the pressure of the gas is increased is generally attributed to the increased density of the gas; but the researches of Schuster, Secchi, and others have indicated that other causes, such as temperature and direction of current, may produce this effect.

At a pressure of 0.160 m. all the lines of hydrogen are nebulous, at 0.080 m. the line F alone is ill defined, and at 0.020 m. all the lines are sharp and well defined.

If now a powerful condenser is interposed in the circuit, the lines C and F widen out, forming an almost continuous spectrum, indicating that the widening of the lines is independent of the pressure.

Neither the intensity of the light, nor the direction of the current in relation to the optical axis of the spectroscope, nor the thickness of the layer of hydrogen observed, exercises any influence on the production of this phenomenon.

Moreover, if while the spectrum of the capillary part of the tube contains nebulous lines, the spectrum of the wide parts of the tube is observed, it is seen that the lines in this spectrum are perfectly well defined. Now, although the pressure in the two parts of the tube must be the same, the temperature in the capillary part is undoubtedly higher, thus proving that the temperature is the principal, possibly the sole, cause of the variation in the width of the lines in a spectrum.
C. W. W.

Spectrum of Magnesium and the Constitution of the Sun. By C. FIEVEZ (*Ann. Chim. Phys.* [5], **23**, 366—372).—The author has investigated the influence which the relative intensity of bright lines in the spectrum of magnesium has on their visibility in observing them alone or projected on a solar spectrum.

He has also studied the change which varied amounts of dispersion and definition make in the number and visibility of the lines in comparing prismatic spectra with those obtained by diffraction. He finds that on gradually diminishing the intensity of the light, the lines, one after another, disappear.

With diffraction spectra, when the slit is made exceedingly narrow, there are eleven lines visible, two being more feeble than the others. The lines b_1 , b_2 , and b_3 are the brightest; and b_1 is seen to be double. On superimposing the solar spectrum, all the bright lines appear to coincide with the corresponding black ones, and in addition, the bright line less refrangible than b_1 , which in general does not seem to have a dark representative, is now seen to be identical with a very fine black line.

On observing the spectrum in a Geissler's tube under diminished pressure, the author finds that with a pressure of 0.60 meter, the line b_4 appears very feeble, and if the solar spectrum be superimposed, it disappears completely, while b_1 and b_2 remain visible. Under 0.70 meter pressure b_4 is invisible, and b_2 is very feeble, while b_1 is clearly defined. If the pressure be now increased, all these lines become distinctly apparent.

The author concludes that the modification in the appearance of the spectrum is caused by a physical alteration, and not by a chemical change such as dissociation, and he considers that the unequal inversion of the magnesium lines is due to a difference of intensity of the rays, and not to a peculiar state of the metal. Consequently, he states that the variations in the solar activity can be deduced from comparable observations of the frequency of inversion and the number of rays inverted.

J. I. W.

Application of Photometry to the Study of Diffusion Phenomena in Liquids. By S. v. WROBLEWSKI (*Ann. Phys. Chem.* [2], **13**, 606—623).—A method for determining the rates of diffusion of saline solutions of ordinary concentration is described, and from the results obtained thereby it is shown that, for the prescribed times and degrees of concentration, *the diffusion constant of sodium chloride decreases with the increase of the percentage of salt dissolved, according to the law of straight lines.* From this it follows that the numerical value of the constant at the same temperature and the same initial state of concentration depends on the duration of the experiment, and that a stationary condition, in which the concentration of the liquid decreases from below upwards according to the law of straight lines, is impossible. The "diffusion constant" of a saline solution is really not a constant at all, since it assumes in each special case a new value.

An exact photometric method is also described for investigating the diffusion phenomena of extremely dilute solutions, by means of which the author hopes to determine the diffusion constant of a liquid into itself.

T. C.

On a New Method of Spectrum Observation. By J. N. LOCKYER (*Proc. Roy. Soc.*, **30**, 22—31).

Note on the Spectrum of Hydrogen. By J. N. LOCKYER (*Proc. Roy. Soc.*, **30**, 31—32).

On the Photographic Spectra of Stars. By W. HUGGINS (*Proc. Roy. Soc.*, **30**, 30—22).

On the Photographic Method of Mapping the Least Refrangible End of the Solar Spectrum; with a Map of the Solar Spectrum from 7600 to 10750. By W. DE W. ABNEY (*Proc. Roy. Soc.*, **30**, 67).

On the Spectra of Magnesium and Lithium. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 93—100).

On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 152—162, and 494—510).

Note on the Spectrum of Carbon. By J. N. LOCKYER (*Proc. Roy. Soc.*, **30**, 335—343, and 461—463).

Note on the Spectrum of Sodium. By W. DE W. ABNEY (*Ibid.*, **32**, 443).

On the History of the Carbon Spectrum. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 490—494).

On the Spectrum of the Flame of Hydrogen. By W. HUGGINS (*Proc. Roy. Soc.*, **30**, 576—580).

On the Spectrum of Water. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 580—582).

Researches on the Action of Organic Substances on the Ultra-violet Rays of the Spectrum. Part III. An Examination of Essential Oils. By W. N. HARTLEY and A. K. HUNTINGTON (*Proc. Roy. Soc.*, **31**, 1—26).

On the Absorption Spectra of Cobalt Salts. By W. J. RUSSELL (*Proc. Roy. Soc.*, **31**, 51—54, and **32**, 258—272).

Reversal of the Lines of Metallic Vapours. No. VIII. Titanium, Chromium, and Aluminium. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 402—406).

On the Iron Lines Widened in Solar Spots. By J. N. LOCKYER (*Proc. Roy. Soc.*, **31**, 348—350).

On the Influence of Molecular Grouping in Organic Bodies on their Absorption in the Infra-red Region of the Spectrum. By W. DE W. ABNEY and R. FESTING (*Proc. Roy. Soc.*, **31**, 416—418).

Investigations on the Spectrum of Magnesium. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 189—203).

On Discontinuous Phosphorescent Spectra in High Vacua. By W. CROOKES (*Proc. Roy. Soc.*, **32**, 206—213).

On the Identity of Spectral Lines of Different Elements. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 225—232).

The Refractive Equivalents of Carbon, Hydrogen, Oxygen, and Nitrogen in Organic Compounds. By J. H. GLADSTONE (*Proc. Roy. Soc.*, **31**, 327—330).

Absolute Measurements of Currents by Electrolysis. By MASCART (*Compt. rend.*, **93**, 50—53).—The author has re-determined the electrochemical equivalent of water by two methods. In the first, water acidified with phosphoric acid was decomposed in a vacuum; the electrodes were fine platinum wires, and the gas evolved was pumped out by means of a mercury pump, and measured in the dry state. Under these circumstances, no sensible traces of H_2 are formed, and there is no loss of gas by condensation on the electrodes, or by diffusion and solution in the liquid. In the second case, the weight of silver deposited from a solution of silver nitrate was accurately determined. In order to eliminate the influence of terrestrial magnetism, the intensity of the current was measured by a special form of electro-dynamometer. Taking the equivalent of silver as 107.93 (Stas), and adopting Weber's units, the electrochemical equivalent of water = 0.009373 mgrm. This number, which is probably exact to at least 0.1 per cent., is practically the same as that given by Weber, 0.009376 mgrm. Adopting B. A. units, a current of 1 Weber electromagnetic intensity will decompose in one second 0.09373 mgrm. of water, or 0.010415 of the equivalent of a body expressed in milligrams. The intensity of current required to decompose a milligram-equivalent of a body in one second is therefore 96.01 Webers.

C. H. B.

Electromotive Force of the Electric Arc. By F. P. LE ROUX (*Compt. rend.*, **92**, 709).—The author proves that the difference of potential between the two carbons of an electric arc is due to a phenomenon of polarisation, the carbon becoming positive to its vapour (which the author believes to constitute the arc) to an extent which increases with the temperature.

C. W. W.

Resistance of Polarised Cells. By E. COHN (*Ann. Phys. Chem.* [2], **13**, 665—669).—Kohlrausch (*Pogg. Ann.*, **138**, 280; and *Jahrbld.*, 290) has shown that quickly alternating currents have no polarising action on a liquid cell, if the electrodes expose a sufficiently large surface, and has applied this fact in determining the specific resistance of a large number of liquids. The author shows that the same principle may also be used for finding the resistance of a cell polarised by a constant current, or in other words, to separate the two constants of the cell, polarisation and resistance. He also shows that hydrogen-polarisation increases, whilst oxygen-polarisation diminishes the resistance of the cells.

T. C.

Development of Polar Electricity in Hemimorphous Crystals by Alteration of Pressure in the Direction of the Asymmetrical Axes. By W. HANKEL (*Ann. Phys. Chem.* [2], **13**, 640—644).—The law enunciated by J. and P. Curie (*Compt. rend.*, **91**, 294), that increase of pressure on cooling, and decrease of pressure

on heating develop similar electrical polarities in hemimorphous crystals, is not general, for whereas some hemimorphs, as, boracite, tourmaline, siliceous calamine, tartaric acid, cane-sugar, and milk-sugar, obey this law, others, as rock crystal, neutral potassium tartrate, and struvite, do not, for in these cases increase of pressure produces the same effect as heating, and diminution of pressure the same effect as cooling.

T. C.

Sound of the Electric Arc. By A. NIAUDET (*Compt. rend.*, 92, 711).—The difference of potential between the two carbons is greater when the arc is silent, smaller when sound is emitted.

The needle of the galvanometer jumps suddenly from one point to another when the noise begins and ceases. While the arc is completely silent, the needle may remain stationary for a considerably time.

C. W. W.

Determination of Chemical Affinity in Terms of Electromotive Force. By C. R. A. WRIGHT (*Phil. Mag.* [5], 9, 237—266, 331—348; 10, 169—196, 261—283, 348—369).—Joule showed many years ago that when a current is passed through a fluid conductor, heat is developed in accordance with the same law as that which he found to hold good with a metallic wire, viz., that the heat produced in a given time is proportional to the square of the current and to the resistance of the conductor; and that if electrolysis takes place, the actual heat developed is less than that required by the law by a quantity equal to that which would be evolved by the recombination of the products of the electrolysis; and consequently that it is possible to determine the heat of formation of a compound by the inverse method of determining the heat evolved during its electrolysis. More recently Sir W. Thomson (*Phil. Mag.*, 1851, 2, 429), has shown that the force of chemical affinity can be expressed in terms of electromotive force.

Faraday's electrolytic laws may be expressed by the equation $n = aqx$, where n = the number of grams of the compound decomposed, q the quantity of electricity passing, a the equivalent of the compound, and x a multiplier independent of the quantity of electricity passing, and of the value of the equivalent of the compound.

When $n = a$, $x = \frac{1}{q}$; i.e., x is the reciprocal of the quantity of electricity required to decompose a gram-equivalent of the electrolyte. x is called the *electrochemical constant*. The "electrochemical equivalent of a substance" is the quantity of substance decomposed by a unit quantity of electricity, i.e., the value of $\frac{n}{q}$ ($= ax$), whilst the "electrochemical equivalent of an element," in reference to such a compound, indicates the quantity of that element evolved during the electrolysis of that compound by a unit of electricity. If b be the equivalent of the element in reference to the compound, the equivalent of the latter being a , then the electrochemical equivalent of the element in reference to the compound is $\frac{n}{q} \cdot \frac{b}{a}$ ($= bx$).

In the passage of electricity between the two electrodes, work is done, not only in decomposition, but also as heat; by determining the amount of the latter, however, that due to decomposition may easily be found; thus, if h gram-degrees are developed during the decomposition of n grams of substance of electrochemical equivalent ax by the transfer of a quantity of electricity q , and if E represent the total potential difference existent between the electrodes, the total work done in the electrolytic cell is Eq , of which hJ is done as heat. Hence $Eq - hJ$ is done as chemical decomposition. Let this = eq , where e is the E.M.F. representing the chemical affinity to be measured; then

$$(x) \quad e = E - \frac{hJ}{q} = E - hJ \frac{ax}{n},$$

$$\text{since} \quad q = \frac{n}{ax}.$$

The entire change taking place is not, however, produced by the direct current alone, but also to some extent by physical changes of state and by secondary actions, so that the value of e thus deduced, although representing the E.M.F. corresponding to the nett work done, and consequently representing the affinity between the ultimate products in the original compound, is not necessarily a measure of the tendency to combine together of the substances primarily formed by the electrolytic decomposition.

By the use of the equation (x) the author has calculated the E.M.F. representing the amount of work corresponding to the sum of the chemical and physical changes which occur when the current from a Daniell's cell is passed through a voltmeter placed in a calorimeter, the average difference of potential between the plates of the voltmeter being determined by means of a quadrant electrometer.

In the case of water acidulated with 22 per cent. of H_2SO_4 the mean value of $E - hJ \frac{ax}{n}$ for 18 experiments, with varying battery power and time, was 1.5×10^8 . Corrections were introduced for the heat absorbed by the vaporisation of the water carried away by the evolved gases and the work necessary to separate the water decomposed from the sulphuric acid.

The experiments tend to show that the value of J , as determined by Joule in 1867 by the electric current method, is about 0.5 per cent. too low, owing to three sources of error, viz., the higher mean temperature of the wire compared with that of the calorimeter, the increased resistance of the wire caused by the coating of varnish applied to it, the greater heating of the B.A. unit coil, the wires of which were imbedded in solid paraffin, compared with the experimental wire which was placed in water. The experiments also show that where a current has to be passed through a wire for any length of time, an error will be caused by the increased resistance of the wire, due to its being heated to a temperature above that of the medium in which it is placed. The author also finds that conduction without electrolysis does not take place, and that Faraday's law is true for excessively minute currents as well as for those of considerable mag-

nitude. With very feeble currents, however, and with certain electrolytes, *e.g.*, water, the quantity of products of decomposition actually collected after a given time, does not absolutely correspond with the quantity of electricity that has passed. This is due to the "diffusion discharge" produced (in the case of water) by the diffusion towards the - electrode of water containing dissolved oxygen, and towards the + electrode of water containing dissolved hydrogen. When the amount of suppression due to this cause is determined and added to the observed amount of decomposition, the total corresponds exactly with the quantity of electricity which has passed.

In the electrolysis of acidulated water, until the sources of loss of hydrogen other than "diffusion discharge" are eliminated, the counter E.M.F. set up when a given steady current traverses a voltmeter is short of its maximum value of that current, and a deficiency of hydrogen is simultaneously observed: whilst on breaking circuit, the rate of fall of the polarisation of the electrodes is more rapid than its minimum value for that current. On the other hand, as soon as the counter E.M.F. reaches its maximum, the deficiency in hydrogen disappears (after correction for diffusion discharge), and the rate of fall of the polarisation, after breaking circuit, reaches its minimum. The more completely the sources of loss are eliminated, the more nearly does the counter E.M.F. set up approach its maximum, the less is the deficiency in the hydrogen collected, and the more nearly does the rate in fall of polarisation approach its minimum.

A theory is enunciated and partly demonstrated, which reconciles the hitherto apparently contradictory numerical values obtained by previous observers for the counter E.M.F. set up during electrolysis, the "subsequent polarisation" existing after the rupture of the current, and the E.M.F. of gas batteries. In accordance with this theory, the relationships between the current flowing and the counter E.M.F. set up in a cell, are expressed by

$$e = E + [\Sigma\{(1 - n)H\} - \Sigma(nh) - \Sigma(H)]\chi J.$$

In the case of all the electrolytes examined, the value of e was found to increase as the current increased, but at a less rapid rate.

So long as the rate of flow per unit of area of electrode surface remains the same, the value of e is constant. With a given current the value of e is diminished by increasing the electrode surface. The values of e depend on the material of which the electrodes are made, carbon giving higher values than platinum, and platinum than gold. In the case of acidulated water, rendering the solution more dilute increases the value of e , as does also a rise of temperature.

The above formula, in conjunction with experimental determinations of the variations in the values of e under various conditions, explains the leading facts connected with counter E.M.F. polarisation and the E.M.F. of gas batteries, and accounts for the possibility, under certain conditions, of decomposing an electrolyte with a less battery E.M.F. than corresponds to the work done in splitting it up into the final products, and also indicates that the E.M.F. of a Daniell's cell is not constant, but is less the greater the current it generates, to such an extent that with currents of very great magnitude a diminution in

E.M.F. to the extent of several per cent. is brought about, and that, in consequence, certain of the methods in use for determining the E.M.F. of cells and their internal resistance are, for certain kinds of cells, incorrect, as they are based on the assumption that the E.M.F. of the cell is constant.

By the above formula and the experimental determination of the causes which make e vary, &c., information can be deduced as to the amount of energy with which gases are condensed upon the surface of solids, and in particular as to the amount of energy requisite to break up an electrolyte into nascent products solely and by conjoining this determination with that of the methods for finding the E.M.F. corresponding with the energy requisite to break it up into the final products, information can be attained concerning the affinity of the constituents of the electrolyte and the variations of that affinity, according as the constituents are nascent, or in their ordinary free state.

T. C.

Deposition of Copper on Iron in a Magnetic Field. By I. REMSEN (*Amer. Chem. J.*, **3**, 157—163). The author has studied the mode of deposition of copper from a solution of its sulphate contained in a shallow vessel of thin iron placed upon the poles of a magnet,—and finds, as a general result of his experiments, that the deposited copper is arranged in ridges around the poles, in directions at right angles to the lines of force, and consequently coincident with the lines marking the equipotential surfaces. Further, the outlines of the poles of the magnet are always sharply defined on the plate, as along these lines a portion of the iron of greater or less width is left unacted on. The question as to whether these effects are due to the action of the magnet on the iron plate, or on the liquid, or on both, remains to be decided by further experiments.

H. W.

Chemico-electric Relations of Metals on Solutions of Potassium Salts. By G. GORE (*Proc. Roy. Soc.*, **30**, 38—49).

Studies on the Electric Arc. By J. DEWAR (*Proc. Roy. Soc.*, **30**, 85—93).

Notes on Electrolytic Experiments. By J. DEWAR (*Proc. Roy. Soc.*, **30**, 170—172).

Decomposition of Water between Platinum Electrodes by the Discharge of a Leyden Jar. By F. STREINTZ (*Ann. Phys. Chem.* [2], **13**, 644—665).

On the Influence of Electric Light on Vegetation, and on certain Physical Principles Involved. By C. W. SIEMENS (*Proc. Roy. Soc.*, **30**, 210—219 and 293—295).

Effects of Electric Currents on the Surfaces of Mutual Contact of Aqueous Solutions. By G. GORE (*Proc. Roy. Soc.*, **30**, 322).

A Preliminary Account of the Reduction of Observations on Strained Material, Leyden Jars, and Voltameters. By J. PERRY and W. E. AYRTON (*Proc. Roy. Soc.*, **30**, 411—435).

The Electrostatic Capacity of Glass.—By J. HOPKINSON (*Proc. Roy. Soc.*, **31**, 148).

Thermo-electric Behaviour of Aqueous Solutions with Platinum Electrodes. By G. GORE (*Proc. Roy. Soc.*, **31**, 244—250).

Experiments on Electric Osmose. By G. GORE (*Proc. Roy. Soc.*, **31**, 253—257).

Electric Currents caused by Liquid Diffusion and Osmose. By G. GORE (*Proc. Roy. Soc.*, **31**, 296—300).

Experimental Researches into Electric Distribution as manifested by that of the Radicles of Electrolytes. By A. TRIBE (*Proc. Roy. Soc.*, **31**, 320—322).

Dielectric Capacity of Liquids. By J. HOPKINSON (*Proc. Roy. Soc.*, **31**, 347).

Influence of Voltaic Currents on the Diffusion of Liquids. By G. GORE (*Proc. Roy. Soc.*, **30**, 322 ; **32**, 56—85).

Determination of the Ohm in Absolute Measure. By LORD RAYLEIGH and A. SCHUSTER (*Proc. Roy. Soc.*, **32**, 104—142).

Refraction of Electricity. By A. TRIBE (*Proc. Roy. Soc.*, **32**, 435—443).

Specific Heat of Organic Compounds and its relation to the Molecular Weight. By M. A. v. REIS (*Ann. Phys. Chem.* [2], **13**, 447—464). The specific heats of the various liquids were determined at several different temperatures, and from the values so obtained the specific heat between 20° and the boiling point was calculated by means of the equation $C_1 = K + a(T + T_1) + b(T^2 + TT_1 + T_1^2)$, in which C_1 is the specific heat between the two temperatures T and T_1 , and K , a , and b are constants depending on the nature of the liquid. The specimens employed were those used by Brühl in the determination of the specific refractions. Several tables of results are given in the original memoir, from which the following general conclusions are drawn:—(1.) The difference between the molecular heats of homologous compounds is quite regular, being about 8.0 between 20° and the boiling point, or 7.5 between 20° and 100°. The alcohols, however, are exceptions, showing a difference of about 9.7 and 8.5 respectively. (2.) Isomeric bodies of similar constitution have the same molecular heat, whilst those of dissimilar constitution have different molecular heats. (3.) Compounds which differ from one another in amount of carbon or hydrogen, &c., also show corresponding regular differences in molecular heat, the observed exceptions being probably

due to compounds being compared which have not an analogous constitution.

As the data to hand are not yet sufficient to allow of any final conclusion being drawn, the author is engaged in further determinations.

T. C.

Iron Chlorides. By P. SABATIER (*Compt. rend.*, **93**, 56—58).—*Ferrous Chlorides.*—Ferrous chloride is less soluble in hydrochloric acid than in water. When warm concentrated hydrochloric acid is saturated with anhydrous ferrous chloride, the liquid on cooling deposits slender transparent pale-green needles of the composition $\text{FeCl}_2 + 2\text{H}_2\text{O}$, which do not alter in a vacuum. The white compound obtained by the efflorescence of the ordinary hydrate, $\text{FeCl}_2 + 4\text{H}_2\text{O}$, in a vacuum has the same composition. The heat of solution of $\text{FeCl}_2 + 2\text{H}_2\text{O}$ at about $20^\circ = +8.72$ cal.; that of $\text{FeCl}_2 + 4\text{H}_2\text{O}$ at $17.5^\circ = +3.32$ cal. From these numbers it follows that—

FeCl_2 (anhydrous) + $2\text{H}_2\text{O} = \text{FeCl}_2 + 2\text{H}_2\text{O}$	
(solid water) develops	+ 6.92 cal.
Or for each mol. H_2O develops.....	+ 3.46 „
$\text{FeCl}_2 + 2\text{H}_2\text{O} + 2\text{H}_2\text{O} = \text{FeCl}_2 + 4\text{H}_2\text{O}$	
(solid water) develops	+ 2.52 „
Or for each mol. H_2O develops.....	+ 1.26 „

The development of heat is greatest in the first stages of hydration.

Ferric Chlorides.—A concentrated solution of ferric chloride evaporated slowly at ordinary temperatures deposits hard, deliquescent, reniform masses of lemon-yellow crystals of the hydrate $\text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, which can also be obtained in opaque, yellow rhombic plates. In a vacuum, these crystals at first form a brown liquid, but finally yield bulky, translucent, deep red, extremely deliquescent crystals of the hydrate $\text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O}$. The heat of solution of $\text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O}$ at $18^\circ = +42.0$ cal., that of $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ at $20.8^\circ = +11.28$ cal. It follows therefore that—

Fe_2Cl_6 (anhydrous) + $5\text{H}_2\text{O} = \text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O}$	
(solid water) develops	+ 14.2 cal.
Or for each mol. H_2O develops	+ 2.84 „
$\text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O} + 7\text{H}_2\text{O} = \text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$	
(solid water) develops	+ 20.72 „
Or for each mol. H_2O develops.....	+ 2.96 „

The heat developed by each successive mol. H_2O is practically constant, but is apparently slightly higher with the first hydrate than with the anhydrous chloride.

When a current of dry hydrochloric acid gas is passed over dry crystals of the hydrate $\text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O}$, it is absorbed, with development of heat, and a liquid is formed which is at first red-brown, but finally greenish-yellow. When cooled, this liquid deposits yellowish, translucent, rectangular lamellæ of a hydrochloride of ferric chloride. The crystals melt at ordinary temperatures, and the liquid when exposed under a bell-jar with potassium hydrate loses all its hydrochloric acid, and is converted into a mass of crystals of $\text{Fe}_2\text{Cl}_6 + 5\text{H}_2\text{O}$. This

hydrochloride has not yet been isolated. The increased solubility of ferric chloride in presence of hydrochloric acid indicates that it exists in concentrated acid solutions.

C. H. B.

Effects of Heat on the Chloride, Bromide, and Iodide of Silver, and on some Chlorobromiodides of Silver. By G. F. RODWELL (*Proc. Roy. Soc.*, **31**, 291—295).—An elaborate paper on the expansion by heat of these compounds was published by the author in 1877 (*Proc. Roy. Soc.*, **25**, 280—303), and in the present paper the values then obtained are corrected according to the new determinations of the melting points of these bodies made by Carnelley's method (this *Journal*, 1878, *Trans.*, 273), these values being in all cases higher than those formerly adopted by the author. The corrected values of the volumes of the several silver-compounds are given in tables in the present paper; also in *Watts's Dictionary of Chemistry*, **8**, pp. 1800, 1801. A comparison of them leads to the following general results:—

The expansion-coefficients of silver chloride and bromide are a little higher than those of the most expansible metals (lead and zinc), and the bromide has a higher coefficient than the iodide. The iodide, on the other hand, has long been known to exhibit certain anomalies, contracting through a certain range of temperature on heating. With regard to these anomalies the following facts have been established. When a mass of the molten iodide is left to cool, the following effects may be observed:—(α.) At the moment of solidification a considerable contraction takes place. (β.) The solid on further cooling undergoes slight and regular contraction after the manner of solids in general, till it reaches a temperature of 142° , when it undergoes a sudden and violent expansion, passing at the same time from the amorphous to the crystalline state. (γ.) After this, the mass on further cooling undergoes slight expansion. The solid iodide exists in two allotropic modifications, being yellow, flexible, and transparent above 142° , whilst at 142° it changes to a pale-green, opaque brittle substance.

Chlorobromiodides.—(1) $\text{Ag}_3\text{IBrCl}_2$; (2) Ag_3IBrCl ; (3) $\text{Ag}_4\text{I}_2\text{BrCl}$; (4) $\text{Ag}_5\text{I}_3\text{BrCl}$; (5) $\text{Ag}_6\text{I}_4\text{BrCl}$. These bodies exhibit the following thermic phenomena:—i. They contract from 124° to 133° , and consequently have two points of similar density. ii. While the contraction of silver iodide begins at 142° and ceases at 145.5° , the chlorobromiodides begin to contract 18° lower, and cease to contract at 12° lower. iii. Their densities are in all cases above the mean of those of their constituents. iv. Their melting points are in all cases lower than those of their constituents: thus No. 3 melts at 326° , viz., 201° lower than the iodide of silver, which constitutes 52 per cent. of its weight. v. The melting points diminish from No. 1 to No. 3, and increase from No. 3 to No. 5. vi. The contraction undergone by some of the chlorobromiodides is greater than that of the iodide itself, although it is associated with two bodies so expansible as the chloride and bromide, while, on the other hand, No. 1 has during certain ranges of temperature a higher expansion-coefficient than either of its components.

H. W.

Expansion-coefficients of Lead Iodide and of an Alloy of Lead Iodide with Silver Iodide. By G. F. RODWELL (*Proc. Roy. Soc.*, **32**, 23—25).—Lead iodide has three coefficients of expansion, the cubical expansions for 1° being as follows:—

Temperature	0—205°	205—253°	253° (m. p.)
Expansion-coefficient.....	·00008317	·0006378	·000180

The rate of expansion between 205° and 253° is unusually high.

Lead-silver iodide, $\text{PbI}_2\cdot\text{AgI}$, expands slowly between 0° and 118°, with a cubical coefficient of 0·0000306; then for a few degrees (118—124°) it simply absorbs heat without expanding or contracting. At 124° it begins to contract, the contraction on further heating going on up to 139°. Between 139° and 144° heat is again absorbed without alteration of volume, and above 144° the double iodide expands somewhat rapidly with a coefficient of 0·000115.

This compound has the same density at three different temperatures, viz., 0°, 130°, and 282°. Although it contains only 33·794 per cent. AgI , it contracts as much during cooling as the silver iodide itself; and whereas the latter begins to contract at 142°, and ceases at 145·5°, the double iodide begins to contract at 18° (*i.e.*, lower by 124°), and ceases to do so at 6·5° lower. The harsh sounds emitted by the double iodide during cooling, and the tremors simultaneously propagated through the mass, show that violent molecular agitation is going on during the passage of the silver iodide from the amorphous plastic to the brittle crystalline state, within the mass of lead iodide. The melting point of the double iodide is 125° lower than that of silver iodide, which constitutes one-third of its weight, whilst it is only 19° higher than that of the lead iodide, which constitutes two-thirds of its weight.

H. W.

Preliminary Notice on the Existence of Ice and other Bodies in the Solid State at Temperatures far above their ordinary Melting Points. By T. CARNELLEY (*Proc. Roy. Soc.*, **31**, 284—291).

On the Thermal Conductivity of Water. By J. T. BOTTOMLEY (*Proc. Roy. Soc.*, **28**, 462; **31**, 300).

On Buff's Experiments on the Diathermancy of Air. By J. TYNDALL (*Proc. Roy. Soc.*, **30**, 10—20).

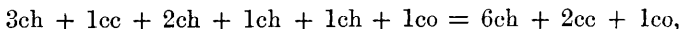
On Heat-conduction in Highly Rarefied Air. By W. CROOKES (*Proc. Roy. Soc.*, **31**, 239—244).

Action of an Intermittent Beam of Radiant Heat on Gaseous Matter. By J. TYNDALL (*Proc. Roy. Soc.*, **31**, 307—317, and 478—479).

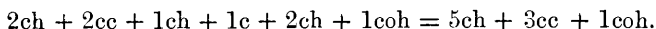
Heat of Combustion of certain Alcohols and Aldehydes of the Fatty Series. By LOUGUININE (*Bull. Soc. Chim.* [2], **36**, 145—149).—The heat of combustion of valeraldehyde, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHO}$, is 742,157 cals., and that of its isomeride, ethyl-vinyl carbinol, is 753,214 cals., the difference being 11,057 cals. Nearly the same dif-

ference exists between the heats of combustion of cœnanthaldehyde, 1,062,596 and of its isomeric alcohol in the allyl series, 1,072,562.

For homologues lower in the series, the differences increase, and it is generally the case that the heat of combustion of the unsaturated alcohol exceeds that of the isomeric aldehyde; *i.e.*, the aldehydes require a greater expenditure of heat in their formation. This fact is explained not only by the difference in structure, but by the inequality of the linkings; thus in propaldehyde (heat of combustion 426,313 cal.), $\text{CH}_2\text{Me.CO.H}$, the number of linkings are—



and in its isomeride allyl alcohol (441,219 cal.), $\text{CHCH}_2.\text{CH}_2.\text{OH}$, the linkings are—



The difference between the heats of combustion of valeric and cœnanthylic aldehydes is 320,439 cal., or 160,220 cal. for each CH_2 group, which value corresponds closely with those found in other homologous series.

The heat of combustion of menthol is approximately 1,524,284, that of allyl dipropyl carbinol 1,344,993.

The heat of combustion of benzyl-methyl carbinol (b. p. 179.5°) is 1,262,105 cal., which agrees within one-third per cent. with the value assigned by Favre and Silberman.

The differences between the heats of combustion of the two series of alcohols are—

		Difference.
$\text{C}_3\text{H}_8\text{O}$	480,313 }	37,663
$\text{C}_3\text{H}_6\text{O}$	442,650 }	
$\text{C}_4\text{H}_{10}\text{O}$	636,706 }	36,578
$\text{C}_4\text{H}_8\text{O}$	600,128 }	
$\text{C}_5\text{H}_{12}\text{O}$	793,923 }	40,709
$\text{C}_5\text{H}_{10}\text{O}$	753,214 }	
$\text{C}_6\text{H}_{18}\text{O}$	1,262,105 }	32,065
$\text{C}_6\text{H}_{16}\text{O}$	1,230,040 }	

The mean of these differences is about 36,800 cal., which is approximately the heat of combustion of 2 atoms of hydrogen. L. T. O'S.

Glycollic Ether and Ethylene Oxides. By BERTHELOT (*Compt. rend.*, **93**, 118—124).—*Ethylene Oxide*, $\text{C}_2\text{H}_4\text{O}$, b. p. 13.5 . Heat of combustion at constant volume = $+307.5$ cal.; at constant pressure 308.4 cal.; heat of evaporation, 6.1 cal.; heat of solution in 160 parts of water at 13° = $+1.5$ cal.; heat of formation from its elements, gas = $+17.7$ cal., liquid, $+23.8$ cal., in solution, $+25.3$ cal. The transformation of ethylene into ethylene oxide by direct oxidation, if this reaction could be realised, would develop $+33$ cal., practically half the amount developed by the formation of aldehyde under the same conditions. The hydration of ethylene oxide with production of glycol develops $+18.9$ cal., a number nearly equal to

the heat of hydration of sulphuric anhydride and barium oxide, much greater than that of the conversion of ethylene into alcohol, C_2H_6O , and still greater than that of the conversion of ethyl ether into alcohol. When the vapour of ethylene oxide is heated to dull redness, a volatile liquid, probably aldehyde, is first formed, and finally it splits up into equal volumes of carbonic oxide and methane, which together occupy twice the volume of the original vapour. Aldehyde splits up in the same manner. Since as a rule the loss of energy is greater when hydrocarbons are converted into aldehydes and acids than when they are converted into alcohols and ethers, the heat of formation of aldehyde should be greater than the heat of formation of ethylene oxide, and this is really the case. C_2 (diamond) + $H_4 + O =$ ethylene oxide (gaseous), develops + 17.7 cal. = aldehyde (gaseous), develops + 50.5 cal. This fact explains the greater chemical activity of ethylene oxide and its extreme tendency to form polymerides. The transformation of ethylene oxide into aldehyde would develop + 32.8 cal., the change of function being accompanied by loss of energy without change in the degree of condensation. This change apparently takes place under the influence of heat, as mentioned above, and also under certain conditions of the nascent state, for the action of zinc chloride on glycol yields aldehyde and not ethylene oxide. This latter fact shows that dehydrations or hydrations by the action of metallic chlorides or other reagents are of little value in determining the constitution of isomerides, and that thermal phenomena are of the highest importance, the constitution of two isomerides being more closely analogous the less the amount of heat developed by the transformation of one into the other. Since aldehyde can be formed from ethylene by direct oxidation, it ought really to be regarded as the first oxide of ethylene, acetic acid being the second. As a matter of fact, the two degrees of oxidation develop an amount of heat proportional to the number of oxygen-atoms fixed, viz., + 65.9 cal. for aldehyde, and + 131.1 cal. for acetic acid. Ethylene oxide is not formed directly from ethylene, because its heat of formation is less than that of aldehyde. Its conversion into aldehyde is analogous to the conversion of chromic, ferric, and other oxides into isomeric modifications.

C. H. B.

Heat of Formation of Explosives. By SARRAU and VIEILLE (*Compt. rend.*, 93, 213—215, and 269—271).—The heat developed by the decomposition of an explosive is a quantity of the first importance in calculating theoretically the maximum amount of work which it can do. The actual determination of this quantity is however a matter of difficulty, since the nature of the decomposition depends on the conditions under which it takes place, and consequently the amount of heat developed also varies. If, however, the heat of formation of the compound, and the composition and heat of formation of the products of decomposition are known, the heat developed by the decomposition can be calculated, for it will be equal to the excess of the heat of formation of the products above that of the original compound. In order to determine the heat of formation, it is necessary to know the actual heat developed by the combustion of the substance, the composition of the products, and their heats of formation. The heat of formation of

the explosive is equal to the difference between the heat of formation of the products of the combustion and the heat developed by the combustion. In order to entirely convert the explosive into simple products, and thus avoid the errors due to incomplete combustion, the authors burn the explosive in an excess of oxygen, and determine the amount of heat developed, and the volume and composition of the gases produced. In this way they have determined the heat of formation of the principal explosives, with the following results:—

Nitro-glycerol.—Heat of formation 94·0 cals. The number calculated from the heat of combustion of glycerol as determined by Louguinine, and the heat of formation of nitric acid and its action on glycerol as determined by Berthelot is 96·0 cals.

Nitro-mannitol.—Heat of formation, 161·5 cals.

Gun-cotton, $C_{24}H_{29}N_{11}O_{42}$.—Heat of formation, 639·5 cals.

Potassium Picrate.—Heat of formation, 117·5 cals. From this value it may be calculated that the action of each molecule of nitric acid on phenol, in forming trinitrophenol, develops 34·0 cals. Berthelot has found that in the formation of mono- and di-nitrobenzenes, each molecule of nitric acid develops 36·0 cals.

Ammonium Picrate.—Heat of formation, 80·1 cals.

By exploding a mixture of gun-cotton and ammonium nitrate, the authors have determined the heat of formation of the latter, and have obtained the value + 89·0 cals. Berthelot found + 87·9 cals.

C. H. B.

Density and Molecular Volume of Certain Acetates. By H. SCHRÖDER (*Ber.*, 14, 1607—1616).—The author has determined the specific gravities and molecular volumes of the following salts:—

	S.	V.
Sodium acetate + $3H_2O$	1·431	95·0
Anhydrous sodium acetate	1·524	53·8
Silver acetate	3·259—3·222	51·3—51·8
Barium acetate + $3H_2O$	2·021	152·9
Anhydrous barium acetate	2·468	103·3
Strontium acetate	2·099	97·9
Lead acetate + $3H_2O$	2·539	149·3
" " anhydrous.....	3·251	99·96
Mercuric acetate.....	3·270	97·2
Copper acetate + H_2O	1·882	106·1
Anhydrous copper acetate.....	1·929	94·05
Nickel acetate + $4H_2O$	1·747	143·0
" " anhydrous.....	1·798	98·4
Cobalt acetate + $4H_2O$	1·704	146·1
Magnesium acetate + $4H_2O$	1·454	147·3
" " anhydrous	1·420	99·9
Zinc acetate + $2H_2O$	1·735	126·2
" " anhydrous	1·840	99·5
Manganese acetate + $4H_2O$	1·589	154·2
" " anhydrous ..	1·745	99·1
Cadmium acetate + $2H_2O$	2·009	132·6
" " anhydrous....	2·341	98·2

A comparison of these numbers shows that the hydrogen of acetic acid can be replaced by calcium, strontium, lead, mercury, nickel, magnesium, zinc, manganese, or cadmium, without effecting any appreciable change in specific volume.

The molecular volumes of the acetates are generally identical with those of the corresponding sulphates: hence it follows that they are multiples of the stere 5.52, *e.g.*, nickel acetate, $C_4H_6Ni_2O_4 \cdot H_2O_4 = 26 \times 5.52 = 143.52$.

W. C. W.

Aggregation of Small Particles. By E. HILGARD (*Bied. Centr.*, 1881, 220—223).—Under the influence of moderate motion, small particles suspended in water have a tendency to coalesce, and form larger aggregates. This is easily seen in the following experiment. A few grams of any powder of the same hydraulic worth of 1 mm. per second are introduced into a glass tube placed in a slanting position and narrowed to a fine jet at the lower end.

A stream of water is now allowed to enter through the fine opening, the motion of the water not exceeding 1 mm. per second, so that none of the powder is carried to the upper opening, but is carried round in small circles. After 10—15 minutes the velocity of the water may be increased four or five times, without any of the sediment being carried up. This is due to the small particles under the influence of the slight motion having aggregated into larger flakes, consisting each of twenty or thirty of the original particles, and requiring strong agitation or boiling for their disintegration. The tendency towards aggregation varies inversely with the size of the particles and the temperature. Alcohol, ether, caustic or carbonated alkalis tend to retard aggregation, whilst neutral salts and acids tend to promote it. This explains why the alkaline soils in California are so hard to work.

J. K. C.

Relations between Dust, Fog, and Clouds. By J. AITKEN (*Bied. Centr.*, 1881, 361—362).—Two large glass receivers were filled the one with common air, and the other with air which had been freed from dust by filtration through cotton wool, and into each of these a steam jet was introduced; in the first the ordinary cloudy form of steam condensation appeared, while the filtered air remained unaltered and perfectly transparent. From these experiments it is seen that the particles of steam do not aggregate together by themselves, but require some solid or liquid body around which to condense. If there is much dust in the air, there can only be a small quantity of water condensed on each particle, the latter are therefore not heavily weighted, and remain suspended in the air as fog or clouds. If on the other hand the quantity of dust present is small, the moisture is precipitated to the earth in the form of fine rain. Among the sources of atmospheric dust the author mentions salt carried from the sea, and meteoric fragments.

J. K. C.

On the Solubility of Solids in Gases. By J. B. HANNAY and J. HOGARTH (*Proc. Roy. Soc.*, 30, 178—188, and 484—490).

On the Absorption of Gases by Solids. By J. B. HANNAY (*Proc. Roy. Soc.*, **32**, 407).

Viscosity of Gases at High Exhaustions. By W. CROOKES (*Proc. Roy. Soc.*, **31**, 446—458).

On the Critical State of Gases. By W. RAMSAY (*Proc. Roy. Soc.*, **30**, 323—329, and **31**, 194—206).

On the Limit of the Liquid State. By J. B. HANNAY (*Proc. Roy. Soc.*, **31**, 520—523).

On a Fourth State of Matter. By W. CROOKES (*Proc. Roy. Soc.*, **30**, 469—473).

On Chemical Repulsion. By E. J. MILLS (*Proc. Roy. Soc.*, **30**, 68—70).

Action of Sulphuric Acid recently Heated to 320° on Oils. By E. J. MAUMENÉ (*Compt. rend.*, **92**, 721).—Two series of experiments were made, one with various samples of linseed oil and ordinary sulphuric acid, the other with the same acid heated to 320°, and used immediately after cooling. In every case the temperature obtained was 80° to 90° higher with the recently heated acid than with the ordinary acid. The differences of temperature obtained with different samples of oil are very decided.

The author thinks that this influence of heating is very general, and that some of the results obtained in thermochemistry may be inexact, in consequence of the neglect of this influence. C. W. W.

Velocity of Propagation of Inflammation in Explosive Gaseous Mixtures. By MALLARD and LE CHATELIER (*Compt. rend.*, **93**, 145—148).—The exact measurement of the velocity of the propagation of inflammation is very difficult, for if the non-ignited portions of the gaseous mixture do not remain at rest, the velocity of propagation is very largely increased. From this cause the results obtained given in the following table, can only be regarded as approximate within 10 per cent.

Hydrogen and Oxygen.			
			Velocity per second.
H ₂	+	$\frac{1}{3}$ vol. O	17·3 m.
"	+	1 " O	10·0 "
"	+	$\frac{1}{2}$ " H	18·0 "
"	+	1 " H	11·9 "
"	+	2 " H	8·1 "

Hydrogen and air.		Coal-gas and air.	
Hydrogen per cent.	Velocity per second.	Coal-gas per cent.	Velocity per second.
0.20	2.0 m.	0.125	0.83 m.
0.25	2.8 „	0.15	1.00 „
0.30	3.4 „	0.175	1.16 „
0.35	4.1 „	0.20	0.9 „
0.40	4.4 „		
0.50	3.8 „		
0.60	2.3 „		

In mixtures of hydrogen and air the maximum velocity is given by a mixture containing about 10 per cent. more hydrogen than the theoretically most explosive mixture, a result similar to that observed in the case of mixtures of air and marsh-gas, and is due to the higher conductivity of the hydrogen. When the gaseous mixtures are heated, the rate of propagation of inflammation is increased. Within certain limits, the diameter of the tube containing the gases does not affect the velocity, but with very narrow tubes the propagation of inflammation is retarded, and the flame is even extinguished. The flame of a mixture of 3 vols. hydrogen with 7 vols. air is extinguished in a tube 0.9 mm. diameter; that of the most explosive mixture of air and coal-gas in a tube 3.2 mm. diameter.

C. H. B.

Inorganic Chemistry.

Some New Compounds of Hydrobromic and Hydriodic Acids with Ammonia. By L. Troost (*Compt. rend.*, **92**, 715).—The author has succeeded in preparing the bromine and iodine compounds corresponding with the chlorine compounds described in a previous paper (*ibid.*, **88**, 578). The compound BrH_2NH_3 has a dissociation-tension of 90 mm. at -27° , 350 mm. at 0° , and 1,025 mm. at 20° .

The compound BrH_4NH_3 melts at $+6^\circ$, and solidifies at -20° in rhomboidal, strongly depolarising tabular crystals. It is converted into the preceding compound by loss of ammonia. Its dissociation-tension is 160 mm. at -27° , 570 mm. at 0° , and 1,365 mm. at 19.5° .

The compound BrH_7NH_3 melts at -20° , and solidifies at -45° . Its dissociation-tension is 540 mm. at -32° , 1,280 mm. at -10° , and 1,745 mm. at -2.8° .

The dissociation-tension of the compound IH_2NH_3 is 10 mm. at -27° , 57 mm. at 0° , and 940 mm. at 50° .

The compound IH_4NH_3 melts at about -12° , and the liquid remains in a state of superfusion when cooled. Its dissociation-tension is 130 mm. at -27° , 380 mm. at 0° , and 700 mm. at 14.6° .

The third compound, IH_7NH_3 , melts at -28° . Its dissociation-tension is 435 mm. at -29° , 770 mm. at 12.8° , and 1,250 mm. at 0° .

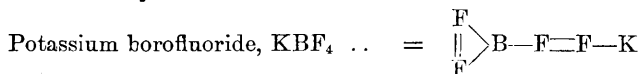
The following is a tabular arrangement of the haloïd compounds of ammonia now known; there are indications of compounds containing still more ammonia.

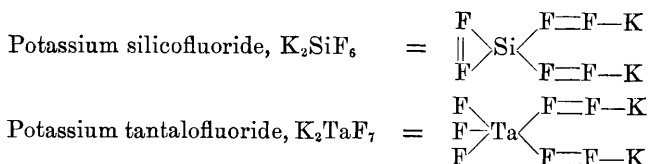
ClH, NH_3	BrH, NH_3	IH, NH_3
"	$\text{BrH}, \text{NH}_3 + \text{NH}_3$	$\text{IH}, \text{NH}_3 + \text{NH}_3$
$\text{ClH}, \text{NH}_3 + 3\text{NH}_3$.	$\text{BrH}, \text{NH}_3 + 3\text{NH}_3$	$\text{IH}, \text{NH}_3 + 3\text{NH}_3$
$\text{ClH}, \text{NH}_3 + 2(3\text{NH}_3)$	$\text{BrH}, \text{NH}_3 + 2(3\text{NH}_3)$	$\text{IH}, \text{NH}_3 + 2(3\text{NH}_3)$
C. W. W.		

Molecular Weight of Hydrofluoric Acid. By J. W. MALLET (*Amer. Chem. J.*, **3**, 189—197).—The question as to whether this compound should be regarded as analogous in constitution to hydrochloric acid or to water, and accordingly whether fluorine should have the atomic weight 19 or 38, has never yet been completely settled. Gore in 1869 (this Journal, **22**, 368), from careful determinations of the molecular volume of hydrogen fluoride prepared by heating silver fluoride in pure and dry hydrogen, found that one volume of hydrogen in uniting with fluorine produced two volumes of gas (just as it does in uniting with chlorine) the gaseous hydrogen fluoride having a density of 10, or a molecular weight of 20. These experiments, in which the temperature of the gas was raised to 95—100°, point to the conclusion that at such temperatures hydrogen fluoride exists as HF, 93·3 and 98·5 per cent. of the theoretical volume having been obtained, after allowance for expansion at the temperature employed; and they further show that the atomic weight of fluorine is 19 and not 38.

Certain other measurements made by Gore at lower temperatures, but still far above the boiling point of the acid (19·5°), distinctly indicate smaller volumes, and therefore greater densities; thus at 59·5° the observed volume was only 85·8 per cent., and at 71° only 88·1 per cent. of that required by theory, and these results are corroborated by the experiments of Mallet, which were made with hydrogen fluoride prepared by the action of the strongest sulphuric acid on pure Greenland cryolite. The gas thus obtained was found to have at 30° a specific gravity = 19·66, and consequently a molecular weight of 39·32, that is to say, double of that which it has at higher temperatures. At these lower temperatures therefore the compound must be represented not by HF, but by H_2F , if $\text{F} = 38$, or by H_2F_2 if $\text{F} = 19$. At higher temperatures, however, dissociation takes place, and the molecule is reduced to HF: hence the formula H_2F_2 is the only one that can correctly represent the constitution of the acid at lower temperatures.

In this double molecule, fluorine may be regarded as a triad, acting in double atoms —F=F— , like the atoms of nitrogen, —N=N— , in the azo-compounds. The author gives a table of the formulæ of a number of fluorine-compounds, artificial and natural, founded on this view, of which the following may be taken as examples:—





In this last formula fluorine appears both as monad and as triad.

H. W.

Diurnal Variation of Carbonic Anhydride in the Air. By G. F. ARMSTRONG (*Proc. Roy. Soc.*, **30**, 343—355).—Up to the present time, our knowledge concerning a diurnal variation in the amount of atmospheric carbonic anhydride may be said to be comprised in the following tabular statement:—

Vols. of CO₂ in 10,000 of Air.

	Day.	Night.	Excess.	
			Day.	Night.
<i>Land-air.</i>				
De Saussure :				
1828	5·037	5·764	—	0·727
1830	4·56	4·81	—	0·250
”	4·45	4·02	0·43	—
P. Truchot :				
1873 { away from vegetation	3·14	3·78	—	0·64
{ near vegetation	4·15	6·49	—	2·34
<i>Sea-air.</i>				
T. E. Thorpe	3·041	2·993	0·028	—

Most of these results give for land-air an excess of carbonic anhydride during the night, which is just what might be expected in consequence of the decomposition of that gas by vegetation during the day. Saussure's last experiments, however, which were made upon country air, and were 13 in number, 8 referring to the day and 5 to the night, gave an excess of 0·43 in favour of the day.

The results of these older experiments being somewhat contradictory, the author was induced to undertake a further examination of the subject. His experiments were made in a garden at Grasmere, situated at the foot of a hill 1,300 or 1,400 feet high, and lying only a few feet above the level of the adjacent lake, which is 208 feet above the sea level. The mode of observation employed consisted in absorbing the carbonic anhydride from a known volume of air by means of baryta-water, and determining the amount so absorbed, by titrating the alkaline liquid with a standard acid solution (Petten-

kofer's method). The results of 27 day and 29 night observations were as follows :—

Night average	=	3.30 vols. CO ₂ in 10,000 vols. of air.
Day average	=	2.96 ,, ,,
<hr/>		
Excess of night over day ..	=	0.34 ,, ,,

To ascertain by direct experiment whether this excess of the night average was due to the action of plants on the air during the day, a healthy geranium plant was suspended day and night alternately in a jar large enough to contain it, the mouth being securely closed. When the plant was removed from the jar, baryta-water was introduced and well shaken, and the carbonic anhydride titrated in the usual manner. These experiments showed that, even if the plant did not actually absorb carbonic anhydride from the air during the day, it at all events exhaled none, whilst at night large quantities were got rid of by exhalation.

Summarising the results of the experiments above described, it may be stated :—1. That the normal amount of carbonic anhydride present in the air of the land is distinctly less than that usually stated, not exceeding 3.5 vols. in 10,000 of air. 2. That plants absorb carbonic anhydride during the day and exhale it during the night, and that vegetation, therefore, affects the quantity of carbonic anhydride present in the air, decreasing it by day and increasing it at night. 3. That from this cause there is, during that part of the year when vegetation is active, at least 10 per cent. more carbonic anhydride present in the air of the open country at night than during the day.

H. W.

Action of Carbonic Anhydride on Potassium Iodide and on Ozonoscopic Papers. By G. PAPASOGLI (*Gazzetta*, 1881, 277—282).

—The results of the author's experiments are summarised as follows :—

(1.) Carbonic anhydride at high temperatures separates hydriodic acid from potassium iodide, but does not act upon the iodate. (2.) At low temperatures, the gas does not decompose pure potassium iodide, but if the iodate be also present even in small quantity iodine is set free. (3.) Light, either diffused or direct, does not decompose either the pure iodide or the mixture of iodide and iodate. (4.) The presence of an alkaline bicarbonate slackens, and may even altogether prevent, the action of carbonic anhydride on a mixture of the two salts.

These results show clearly the importance of using potassium iodide chemically free from iodate in the preparation of ozonoscopic papers, inasmuch as a mere trace of iodate in the iodide, and a small quantity of carbonic anhydride in the air, are sufficient to lead the observer into error in testing for ozone. It is therefore advisable to test the solution of iodide intended for the preparation of ozonoscopic papers, with carbonic acid and starch-paste, before using it for that purpose.

In the course of his experiments, the author observed that the decomposition of potassium iodide is much affected by the quality of the glass of which the containing vessel is made. Green glass is for the most part but little affected by it, but white glass is readily attacked,

so that after prolonged boiling, the distillate is found to contain free iodine, while the residual liquid contains suspended particles of silica and lime, and the receiver when dried appears opaque. H. W.

Sodium Hyposulphite. By A. BERNTHSEN (*Compt. rend.*, **93**, 74—77).—A reply to Schutzenberger (this vol., 682). The author finds that 1 atom of sulphur in the state of hyposulphite is oxidised to sulphuric acid by 3 and not 4 atoms of iodine, and that for each atom of sulphur 1 mol. of copper sulphate is reduced to cuprous oxide. He maintains that the true formula of sodium hyposulphite is $\text{Na}_2\text{S}_2\text{O}_4$ or NaSO_2 , and not NaHSO_2 . C. H. B.

Hyposulphurous Acid. By SCHUTZENBERGER (*Compt. rend.*, **93**, 151—152).—A reply to Bernthsen (preceding abstract).

Some Compounds of Sulphur and Nitrogen. By E. DEMARÇAY (*Compt. rend.*, **92**, 726).—In a previous paper (*ibid.*, **91**, 1066; this vol., p. 222) the author described a body, $\text{S}_4\text{N}_3\text{Cl}$, formed when sulphur chloride is heated with nitrogen sulphide. If the substances react in the cold, however, a black crystalline substance, $\text{S}_6\text{N}_4\text{Cl}_2$, *dichloride of dithiotetrathiazyl*, is formed. It is dissolved by sulphuric acid, with evolution of hydrochloric acid, and is decomposed by heat according to the equation $3\text{S}_6\text{N}_4\text{Cl}_2 = 4\text{S}_4\text{N}_3\text{Cl} + \text{S}_2\text{Cl}_2$. Chloride of sulphur acts on chloride of thiazyl, SNCl , with production of *dichloride of thiodithiazyl*, $\text{S}_3\text{N}_2\text{Cl}_2$, a yellow crystalline body, which is decomposed by sulphuric acid with evolution of hydrochloric acid and production of a fine red solution. By the action of water, a black compound, $\text{S}_3\text{N}_2\text{O}_3$, is produced. Chlorine reproduces chloride of thiazyl. At 100° it decomposes, giving off chlorine and chloride of thiazyl, and leaving a residue of chloride of thiotrithiazyl. A small quantity of a red compound, possibly $\text{S}_3\text{N}_3\text{Cl}$, is also formed.

C. W. W.

Action of Lead Peroxide on Alkaline Iodides. By A. DITTE (*Compt. rend.*, **93**, 64—67).—When hydrated lead peroxide acts on a solution of potassium iodide out of contact with air, iodine is set free, and white brilliant needles of the oxyiodide, $(\text{PbI}_2\text{PbO})_2 + \text{H}_2\text{O}$, are formed. In presence of air, the potassium hydroxide set free absorbs carbonic anhydride from the air, the potassium carbonate formed complicates the reaction, and slightly yellowish needles of the compound $\text{PbI}_2\text{PbO} \cdot \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$ separate out. When heated, the crystals lose water, and melt to a brown liquid, which forms a yellow mass on cooling: the compound is decomposed by dilute acids, carbonic anhydride being given off, whilst the lead oxide dissolves, and a residue of less soluble iodide is left. The same compound may be obtained more readily by passing a few bubbles of carbonic anhydride into a mixture of potassium iodide solution and lead peroxide, or by adding a small quantity of hydrogen potassium carbonate. If too much bicarbonate or carbonic anhydride is added, the compound $2(\text{PbI}_2\text{PbO}) \cdot 3\text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$ is formed. When a current of carbonic anhydride is passed into a mixture of lead peroxide and potassium iodide, the latter being in excess, iodine is set free, and soon all the peroxide is converted

into brilliant needles of either $\text{PbI}_2 \cdot 2\text{KI} + 2\text{H}_2\text{O}$, or if the unaltered potassium iodide and the potassium carbonate formed are present in the necessary proportions, $\text{PbI}_2 \cdot 2\text{KI} \cdot \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$. Both these compounds are decomposed by water. If on the other hand, lead peroxide acts on potassium iodide in presence of an excess of potassium bicarbonate iodine is set free, and a double carbonate, $2\text{PbCO}_3 \cdot \text{K}_2\text{CO}_3$, is obtained as a white crystalline powder. All the compounds previously described are converted into this double carbonate by the action of an excess of hydrogen potassium carbonate. It is evident that the product of the action of lead peroxide on potassium iodide in presence of potassium carbonate varies with the relative proportions of iodide and carbonate. An increase of temperature has the same effect as an increase in the proportion of carbonate present. Similar results were obtained with sodium iodide.

C. H. B.

Note on the Existence of Potassium Thiosulphate in the Solid Residue of Fired Gunpowder. By CAPTAIN NOBLE and F. A. ABEL (*Proc. Roy. Soc.*, **30**, 198—207).—In a former paper, already abstracted in this Journal (1879, Abstr. 992), the authors stated that potassium thiosulphate ("hyposulphite" in the original) constituted from 1 to 6 per cent. of the solid products of the combustion of gunpowder when fired in a closed vessel. Berthelot, on the other hand (*ibid.*, 875), pointed out that this salt could not be a direct product of the explosion, the temperature of which is $2,200^\circ$, inasmuch as it is decomposed at 550° ,—but that it was probably a secondary product formed by the action of sulphurous oxide or nitrous vapours on the sulphide present, after the apparatus had cooled, or by atmospheric oxidation during the removal of the residues from the explosion-vessel, and their preparation for analysis. The authors, in their former experiments, had used copper oxide as the agent for separating the thiosulphate from the sulphide of potassium in the residue, being under the impression that it would simply convert the potassium sulphide into copper sulphide, without exerting any action on the thiosulphate. Debus, however, having pointed out that potassium polysulphides are somewhat readily oxidised to thiosulphate by copper oxide, the authors subjected the monosulphide to the same treatment, and obtained a quantity of thiosulphate equivalent to 11.6 per cent. of the monosulphide used. They, therefore, in their further experiments on fired gunpowder, adopted zinc chloride instead of copper oxide as the agent for separating the thiosulphate from the sulphide in the residues, and then found that only very small quantities of thiosulphate—due, perhaps, to oxidation during the removal from the explosion-vessel—were contained in the residues. Thus, in an experiment with F. G. powder, the quantity of thiosulphate found in the residues, when the separation was effected by zinc chloride, was only 0.07 part per 100 parts of powder exploded, whereas when copper oxide was used, it amounted to 1.56 parts per 100. They therefore conclude that potassium thiosulphate cannot be regarded as a normal constituent of the residue of gunpowder fired in closed vessels, and that Berthelot is correct in regarding this salt as an accidental product, which, if existing occasionally in appreciable amount in the solid matter pre-

vious to its removal from the explosion-vessel, is formed under exceptional conditions, and then only in comparatively small proportions.
H. W.

Decomposition of Sodium Salts by Cupric Hydrate. By D. TOMMASI (*Compt. rend.*, **92**, 453).—Pure precipitated cupric hydrate was placed in a 10 per cent. solution of sodium chloride (neutralised in some cases with acetic acid), and after the lapse of a week, the liberated alkali was estimated. This amounted, in one case, to 0.2772 per cent. of NaHO.

Potassium chloride was decomposed in a similar manner. Precipitated cupric carbonate with sodium chloride gave a notable quantity of sodium carbonate. The temperature in all the experiments was below 9°.
C. W. W.

Solubility of Mixtures of Salts of the Alkali and Alkaline Earth Metals. By H. PRECHT and B. WITTJEN (*Ber.*, **14**, 1667—1675).—The following table contains, in the columns II and III, the amount of potassium chloride and sodium chloride dissolved by water at different temperatures from a mixture of the salts. Columns IV and V show the solubilities of the mixed salts in a 20 per cent. solution of magnesium chloride.

I.	II.	III.	IV.	V.
Temp.	KCl per cent.	NaCl per cent.	KCl per cent.	NaCl per cent.
10°	8.8	20.9	4.2	5.7
20	10.2	20.3	5.1	5.8
30	11.7	19.7	6.0	5.9
40	13.2	19.1	6.9	6.0
50	14.7	18.5	7.9	6.1
60	16.2	17.9	8.9	6.3
80	19.2	16.9	10.9	6.6
100	22.2	15.9	13.0	6.9

When a mixture of potassium sulphate and chloride is treated with water, the solubility of potassium chloride is approximately the same as in pure water. Only a small quantity of the potassium sulphate is dissolved, e.g., 1.32 parts in 100 parts of water at 10°, and 2.53 at 100°.

The solubility of a mixture of barium and sodium chlorides is shown in the following table:—

In 100 parts H ₂ O.			In 100 parts H ₂ O.		
	BaCl ₂ .	NaCl.		BaCl ₂ .	NaCl.
10°	33.9	25.0	60	33.5	31.6
20	33.8	26.4	70	33.6	33.0
30	33.7	27.7	80	33.6	34.3
40	33.6	29.0	90	33.6	35.7
50	33.5	30.3	100	33.6	37.0

W. C. W.

Strontium and Barium Oxychlorides. By ANDRÉ (*Compt. rend.*, **93**, 58—61).—When strontium hydrate is boiled in a highly concentrated solution of strontium chloride, the liquid on cooling deposits nacreous lamellæ of the compound $\text{SrCl}_2 \cdot \text{SrO} + 9\text{H}_2\text{O}$, easily decomposed by water and alcohol. Its heat of solution in dilute hydrochloric acid = + 16.72 cal.; its heat of formation, $\text{SrCl}_2 + \text{SrO} + 9\text{H}_2\text{O}$ (liquid), = + 48.88 cal.; $9\text{H}_2\text{O}$ (solid) = + 36.02 cal. It loses water in a vacuum, forming $\text{SrCl}_2 \cdot \text{SrO} + \text{H}_2\text{O}$, the heat of formation of which, $\text{SrCl}_2 + \text{SrO} + \text{H}_2\text{O}$ (liquid) = + 26.28 cal.; H_2O (solid) + 24.85 cal.

When 200 grams crystallised barium chloride and 60 grams barium hydrate are boiled with 500 grams water, the filtered solution, on cooling, deposits nacreous lamellæ similar to those of strontium oxychloride, and very readily decomposed by water and alcohol. The crystals always have the same composition, $\text{BaCl}_2 \cdot \text{BaO} + 8\text{H}_2\text{O} + (\frac{1}{10}\text{BaO} \cdot 10\text{H}_2\text{O})$, but the author was not able to determine whether they are a mixture of an oxychloride, BaOCl , with barium hydrate or a true combination of 10BaCl_2 with 11BaO . The heat of solution of $\text{BaCl}_2 \cdot \text{BaO} + 8\text{H}_2\text{O}$ in dilute hydrochloric acid, a correction being made for the $\frac{1}{10}\text{BaO} \cdot 10\text{H}_2\text{O}$, regarded as existing in the free state, = + 19.68 cal. Its heat of formation, $\text{BaCl}_2 + \text{BaO} + 8\text{H}_2\text{O}$ (liquid), = + 37.62 cal.; $8\text{H}_2\text{O}$ (solid) = + 26.18 cal. When the crystals are dried in a vacuum the compound $\text{BaCl}_2 \cdot \text{BaO} + 3\text{H}_2\text{O} + (\frac{1}{10}\text{BaO} \cdot \text{H}_2\text{O})$ is obtained. Regarding the barium hydrate as mechanically mixed, the heat of formation of this oxychloride, $\text{BaCl}_2 + \text{BaO} + 3\text{H}_2\text{O}$ (liquid) = + 26.42 cal.; $3\text{H}_2\text{O}$ (solid) = + 22.14 cal.

In the series of the alkaline earths the tendency to form an oxychloride is highest in the case of calcium, and lowest in the case of barium, strontium occupying an intermediate position. C. H. B.

Decipium and Samarium. By DELAFONTAINE (*Compt. rend.*, **93**, 63—64).—The substance which the author described in 1878 as *decipium* is in reality of a mixture of two bodies. The first gives no absorption spectrum, and its oxide has an equivalent of about 130. For this he proposes to retain the name *decipium*. The oxide of the second has an equivalent probably lower than 117, and its solutions give the absorption spectrum previously attributed to decipium, which is identical with that given by Lecoq's samarium. The author therefore proposes to retain the name *samarium* for this second metal. Marignac's $\text{Y}\beta$ is probably identical with samarium, and his $\text{Y}\alpha$ is probably a mixture of decipium and terbium. C. H. B.

Mineralogical Chemistry.

Composition of some New South Wales Coals. By A. LIVERSIDGE (*J. Roy. Soc., N.S.W.*, **14**, 181—212).—This paper exhibits the chemical composition, proximate and ultimate, of certain New South Wales coals—also of the so-called “Kerosene shale” and of one or two other carbonaceous minerals more or less allied to coal. The main object of the examination was to compare the value of the New South Wales coals with that of English and other European coals. In this point of view, the determination of the proportion of sulphur and of ash is of especial importance, inasmuch as a large amount of mineral matter renders a coal worthless, and a high proportion of sulphur renders it unpleasant for domestic consumption, and makes it useless for most manufacturing and metallurgical operations.

The proximate composition and evaporative power of several varieties of New South Wales coal, as determined by the author's experiments, are given in the table (p. 981). The evaporative power was estimated by means of Thompson's calorimeter, for a description of which see *Percy's Metallurgy*, vol. i, p. 541.

The mean percentages of sulphur in various kinds of British coal, according to Playfair and De la Beche, are as follows:—

Welsh.	Derbyshire.	Lancashire.	Newcastle.	Scotland.
1·42	1·01	1·42	0·94	1·45

on the whole, therefore, rather higher than in New South Wales coals.

The percentage of ash in English Newcastle coking coal varies from 0·79 to 2·19 per cent., average 1·68. Nottinghamshire coking coal contains 3·9 per cent., and coal from Blaina, New South Wales, averages 2·63 per cent. In British non-coking coals the percentage of ash is rather higher, viz., in South Staffordshire coal, from 1·55 to 6·44; in South Wales coals from 1·20 to 7·18, and in Scotch coals from 1·43 to 6·75.

The proportion of ash in the New South Wales coals of the northern district is therefore somewhat higher than the average amount in British coal, and in the southern and western districts considerably higher.

Kerosene Shale.—This mineral is not very appropriately named, inasmuch as it does not possess the lamellar or slaty structure of a shale, but rather resembles cannel coal or torbanite. When of good quality it burns readily, like cannel coal, without melting, and emits a luminous smoky flame. When heated in a tube it neither decrepitates nor fuses, but gives off gaseous and liquid hydrocarbons. Colour from brown-black, sometimes with a greenish shade, to full black. Lustre resinous to dull. Fracture usually broad conchoidal. Emits a dull sound when struck. Powder light brown to grey. Streak shining. The mineral usually weathers to a light grey colour, and the surfaces of the joints are often coated with a white film. It is easily cut into

Proximate Composition of New South Wales Coals.

Name of Colliery.	Moisture.	Volatile hydro-carbons.	Fixed carbon.	Ash.	Sulphur.	Sp. gr.	Coke.	Water converted into steam by 1 lb. of coal.
NORTHERN DISTRICT COALS.								
Russell's	1.35	44.09	49.95	2.70	1.41	1.274	52.65	13.21 lbs.
Greta	2.25	39.21	54.41	2.72	1.41	1.287	57.13	13.21 "
Waratah	2.21	36.70	55.82	4.15	1.12	1.303	59.97	14.30 "
Wallsend	2.75	34.17	57.22	4.64	1.22	1.333	61.86	13.21 "
Cardiff Mine	1.85	43.35	49.49	4.94	0.34	1.286	54.43	—
Agr. Assoc. Co.'s Mine, Newcastle	2.20	33.60	57.52	5.35	1.33	1.297	62.87	12.92 "
Anvil Creek	1.74	41.10	47.90	7.80	1.46	1.323	55.70	12.65 "
WESTERN DISTRICT COALS.								
Wallerawang	1.95	27.25	61.86	8.94	—	1.398	70.10	—
Ditto	1.51	33.24	55.74	9.50	—	1.333	65.24	—
Vale of Clwydd	2.10	33.38	53.38	9.80	1.37	1.323	63.18	12.10 lbs.
Lithgow Valley	1.95	34.18	52.31	10.12	1.41	1.329	62.46	12.10 "
Bowenfels	2.36	28.35	56.54	11.40	1.35	1.399	none	12.65 "
Eskbank	2.00	33.55	49.97	12.91	1.57	1.335	62.88	12.65 "
SOUTHERN DISTRICT COALS.								
Nattal	3.28	4.34	87.96	4.41	trace	—	92.37	undet.
Mount Keira	1.15	23.51	64.65	9.70	0.99	1.379	74.35	12.92 lbs.
Berrima	1.70	32.78	53.84	10.40	1.28	1.364	64.24	11.82 "
Mount Kembla	1.50	19.74	67.18	10.72	0.86	1.363	none	13.21 "
Bulli	10.3	23.65	61.61	13.17	0.54	1.471	74.78	12.21 "

shavings. Thin sections under the microscope present a reticulated appearance, the network being black and opaque, and enclosing brown and amber-coloured translucent particles.

The following table exhibits the composition of "Kerosene shale" compared with that of torbanite and other hydrocarbons, the several minerals being arranged in the descending order of their amount of volatile hydrocarbons.

Locality.	Moisture.	Volatile Hydrocarbons.	Fixed carbon.	Ash.	Sulphur.	Specific gravity
K. from Joadja Creek.....	0·44	83·361	8·035	7·075	0·589	1·054
„ Hartley Vale.....	—	82·24	4·97	12·79	—	1·052
„ Joadja Creek.....	0·04	82·123	7·160	10·340	0·337	1·229
„ Joadja Creek.....	1·16	73·364	15·765	9·175	0·536	1·103
Cannel coal, Mold, Flintshire (Percy).....	—	72·08	21·91	6·01	—	—
K. from Murrurundi.....	1·165	71·882	6·467	19·936	0·549	—
Torbanite from Torbane Hill, Edinburgh (H. How)	—	71·17	7·65	21·18	—	1·170
Cannel coal, Scotland (Percy)	—	69·77	10·45	19·78	—	—
Torbanite, Torbane Hill....	0·720	69·695	9·045	20·54	—	—
K. from Greta mine.....	0·48	61·18	25·13	13·21	—	—
Albertite from New Brunswick.....	—	57·490	42·086	0·424	—	1·10
K. from Greta mine.....	1·475	53·798	27·946	15·870	0·911	1·130
Cannel coal, Wigan.....	1·464	45·900	45·519	7·117	—	1·259

Hydrocarbon from the Waratah Mine, Northern District.—This mineral is jet black, highly lustrous, very brittle, breaking into more or less regular four-sided prismatic pieces, the prisms running at right angles to two of the walls of the pipe. Cross-fracture conchoidal. Powder or streak, black. The powdered mineral is insoluble in alcohol, carbon bisulphide, benzene, ether, ammonia, caustic soda, and sodium thiosulphate, but dissolves partially in boiling nitric acid, yielding a brown solution. It is readily inflammable, does not fuse, burns with a smoky luminous flame and disagreeable smell. Swells up but slightly on platinum foil. Sp. gr. 1·30. Hardness about 2.

Proximate Analysis.

Loss at 100°	3·600
Volatile hydrocarbons, &c.	29·174
Fixed carbon.....	63·772
Ash.....	1·064
Sulphur.....	2·380
	<hr/>
	99·990

Ultimate Analysis.

Moisture at 100°	3·600
Carbon	70·246
Hydrogen.....	5·080
Oxygen.....	17·630
Sulphur.....	2·380
Ash	1·064
	<hr/>
	100·000

This hydrocarbon does not quite agree in composition with any mineral hitherto described, but appears on the whole to resemble albertite more closely than any other. Its composition does not lead to any definite formula.

Bog Butter.—A soft, white, unctuous substance, probably a form of adipocere, found between Twofold Bay and Brogo. It resembles fat, but is less greasy; is inclined to crumble to pieces when pressed. Dried at 100° it gave by analysis:—

C.	H.	N.	O.	Ash.
80·648	5·618	5·461	1·553	6·720 = 100
H. W.				

Inorganic Constituents of the Coals of New South Wales.

By W. A. DIXON (*J. Roy. Soc., N.S.W.*, **14**, 163—179).—The coals of this colony naturally divide themselves into three groups, namely those of the Northern, Southern, and Western fields, and the character of the ash follows, as a rule, the same divisions, except that the ash of the coal found at Redhead, 8 miles south of Newcastle, differs from that of the others in its neighbourhood, in containing much less iron and alumina, and a larger quantity of silica. With the coals of the Northern district may be taken a sample from the Clarence River district. The whole of the ashes showed traces of alkalis, carbonic acid, and chlorine, in addition to the constituents estimated, but the quantities were in all cases very minute.

Ash-analyses of Coals from the Northern Fields.

	Newcastle Coal Company Colliery.		Australian Agricultural Company's Colliery.		Co-operative Coal Co., Plattsburgh, near Newcastle.	
	Sp. gr. of coal 1·283. Ash, reddish; 4·76 p. c.		Sp. gr. of coal 1·286. Ash reddish; 4·44 p. c.		Sp. gr. of coal 1·310. Ash, reddish; 4·20 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina	27·21	6·51	22·84	3·45	23·34	5·90
Ferric oxide	11·11	3·02	15·20	trace	9·33	3·17
Lime	1·46	0·61	1·98	—	3·71	—
Magnesia	1·56	0·63	trace	—	1·99	0·49
Sulphuric oxide	0·72	—	0·97	—	0·72	—
Phosphoric „	1·24	—	2·26	—	1·34	—
Silica	—	45·57	—	53·10	—	49·32
Undetermined and loss..	0·36		0·20		0·69	
	43·30	56·34	43·25	56·55	40·43	58·88
	100		100		100	

	Newcastle, Wallsend Colliery.		New Lambton Colliery, near Newcastle.		Ferndale Colliery, Newcastle.	
	Sp. gr. of coal 1·347. Ash, reddish ; 4·28 p. c.		Sp. gr. of coal. 1·291. Ash, red ; 6·72 p. c.		Sp. gr. of coal 1·296. Ash, buff ; 3·84 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina.....	22·25	6·48	15·00	5·56	23·24	6·42
Ferric oxide.....	11·20	3·31	17·72	2·16	9·21	3·44
Lime.....	3·05	0·32	2·26	0·69	2·41	0·24
Magnesia.....	1·31	0·41	2·72	0·37	2·11	0·23
Sulphuric oxide.....	0·83	—	—	—	0·74	—
Phosphoric „.....	1·14	—	1·28	—	1·25	—
Silica.....	—	50·21	—	52·32	—	50·82
	39·78	60·73	38·98	61·10	38·96	61·15

	Waratah Colliery.		Redhead, near Newcastle.		Clarence River.	
	Sp. gr. of coal 1·293. Ash 4·64 p. c.		Sp. gr. of coal 1·325. Ash, grey ; 6·84 p. c.		Ash, grey ; 8·75 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina.....	22·31	4·59	13·59	5·03	22·78	5·13
Ferric oxide.....	8·11	2·31	4·74	1·97	4·01	—
Lime.....	2·41	—	1·96	—	1·26	—
Magnesia.....	0·98	—	0·71	—	0·48	—
Sulphuric oxide.....	0·71	—	0·45	—	0·21	—
Phosphoric „.....	2·29	—	1·72	—	0·96	—
Silica.....	—	56·17	—	69·65	—	65·12
Undetermined and loss..	0·12		0·18		0·05	
	36·81	63·07	23·17	76·65	29·70	70·25
	100		100		100	

For comparison with these results, samples of the roof and floor of the Australian Agricultural Company's seam were analysed. Of the roof, two specimens were much alike, and consisted of a shaly sandstone, containing a small quantity of coaly matter, whilst the third

contained so much of this as to be an impure coal, containing 49 per cent. of ash; this was not analysed further. Of the floors, two specimens were analysed, corresponding with the roof-specimens.

Roof Galley Way.

Percentage of Organic Matter and Water,
9·97.

Analysis of Residue :—

	Sol. in acid.	Insol. in acid.
Alumina	6·68	12·31
Ferric oxide	2·77	—
Lime	0·42	—
Magnesia	1·32	—
Sulphuric oxide	0·21	—
Phosphoric „	0·41	—
Chlorine	trace	—
Silica.....	—	75·56
Undet. and loss.	0·32	—
	11·81	88·19

Floor Galley Way.

Per cent. of Organic Matter and Water,
30·95.

Analysis of Residue ;—

	Sol. in acid.	Insol. in acid.
Alumina	8·26	13·58
Ferric oxide	2·21	—
Lime	0·42	—
Magnesia	0·65	—
Phosphoric oxide	—	—
Silica.....	—	75·12
Undet. and loss .	—	—
	11·54	88·70
	100·24	

Roof Old No. 1 Way.

Percentage of Organic Matter and
Water, 7·70.

Analysis of Residue :—

Alumina	}	11·89
Ferric oxide		
Lime		1·61
Magnesia		0·93
Phosphoric oxide..		0·37
Insoluble		84·73
Undetermined		0·47
		100·00

Floor Old No. 1 Way.

Per cent. Organic Matter and
Water, 4·30.

Analysis of Residue :—

	Sol. in acid.	Insol. in acid.
	4·88	12·43
	2·84	—
	0·53	—
	0·31	—
	0·16	—
	—	78·73
	0·12	—
	8·72	91·16
	100	

From the last four analyses it appears that the phosphoric oxide increases in quantity with the organic matter, and that the quantity of alumina in the soluble portion does not bear to that in the insoluble the same proportion that it does in the coal-ashes. The ratio between the insoluble and soluble alumina in the various analyses of the Northern coals is as follows :—

A. A. Company	1:6·5	Wallsend	1:3·4
Waratah	1:4·8	New Lambton	1:2·7
Clarence River.....	1:4·4	Redhead	1:2·7
Newcastle Company .	1:4·2	Roof Galley Way ..	1:0·5
Co-operative.....	1:3·9	Floor „ ..	1:0·6
Ferndale	1:3·6	„ Old No. 1 Way	1:0·4

These ratios exhibit very great differences, and appear to indicate that the ash-constituents of the coal are not derived simply from admixture of the material of the floor or roof in an unchanged state.

Dana (*Manual of Geology*, 2nd ed., 366 [1874]), infers from the observations of Alderholdt (*Annalen*, **82**, 111) and Church (*Chem. News*, **30**, 37), on the presence of large quantities of alumina in the ashes of lycopodiums, that the alumina present in coal may have been in some measure derived from the ashes of lycopodiaceous plants, such as lepidodendron. The different ratio of soluble to insoluble alumina in the coal-ashes to that in the roof and floor appears to support this view, as we may readily suppose that alumina which has been assimilated by plants, will be more easily soluble than the same earth which has not been assimilated.

The presence of phosphoric acid in coal-ashes has been noticed by Le Chatelier and Leon Durand-Clage (*Bull. Soc. Encourag. de l'Industrie Nationale*, 1873), who found it in the ashes of French coals to the amount of 0·2 to 1·5 per cent., and by Riley, who found from 0·21 to 3 per cent. of it in the ash of Welsh coals (*Percy's Metallurgy*, Fuel, 352). It is evidently a plant-residue, and is present in notable quantity in the strongly-coking Northern coals, which contain a much larger quantity of it than could be introduced by simple admixture of the material of the floor or roof, whilst on the other hand there seems but little probability that it could be removed from either source by solution, and deposited in the coal.

Coals of the Southern District.

	Osborne Wallsend Colliery.		Illawarra Coal Company, Mount Pleasant Colliery.		Bulli Colliery.	
	Sp. gr. of coal, 1·404. Ash, grey, 10 p. c.		Sp. gr. of coal, 1·354. Ash, grey, 8·76 p. c.		Sp. gr. of coal, 1·369. Ash, grey, 11·28 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina	30·31	5·24	34·07	6·50	26·84	7·60
Ferric oxide	8·68	trace	6·03	trace	7·95	—
Lime	1·18	—	0·82	—	0·67	—
Magnesia	trace	—	trace	—	trace	—
Sulphuric oxide	0·34	—	0·51	—	0·31	—
Phosphoric „	trace	—	0·32	—	trace	—
Silica	—	54·76	—	51·19	—	56·93
Undetermined and loss..	—	—	—	0·56	—	—
	40·51	60·00	41·75	57·69	35·77	64·53
	100·51		100		100·30	

	Coal Cliff.		Berrima.		Katoomba.	
	Sp. gr. of coal, 1·378. Ash, greyish- white, 10·80 p. c.		Sp. gr. of coal, 1·408. Ash, greyish- white, 9·40 p. c.		Sp. gr. of coal, 1·400. Ash, greyish- white, 10·04 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina	31·56	3·61	18·61	0·82	35·26	3·23
Ferric oxide	5·33	trace	4·68	—	0·98	—
Lime	0·75	—	0·58	—	trace	—
Magnesia	0·60	—	—	—	0·30	—
Sulphuric oxide	0·31	—	0·13	—	—	—
Phosphoric „	0·29	—	trace	—	0·56	—
Silica	—	57·41	—	75·05	—	59·58
Undet. and loss	0·14		0·13		0·09	
	38·84	61·02	24·00	75·87	37·10	62·81
	100·00		100·00		100·00	

These ashes are distinguished from those of the Northern coals by their smaller proportion of phosphoric oxide, the former giving an average of 1·5, the latter 0·22 per cent. The ratio of the soluble to the insoluble alumina is greater, and the range is also greater, as shown by the following table, in which the quantity of insoluble alumina is taken as unity:—

Berrima	1 : 21·4
Katoomba	1 : 10·9
Coal Cliff	1 : 8·7
Osborne Wallsend....	1 : 5·7
Illawarra	1 : 5·2
Bulli	1 : 3·5

There are no analyses of roofs or floors to compare with these ashes; but both, at all events in the case of the last three coals, are described as sandstones, a name which would scarcely be applied to a rock containing a quantity of alumina equal to that of these coal-ashes. It therefore appears as if the high percentage of alumina in these ashes, the greater part of which is readily soluble, is again due to an original assimilation by the coal-producing plants.

Coals of the Western District.

	Vale of Clwydd Colliery.		Eskbank.		Lithgow Valley.	
	Sp. gr. of coal 1·328. Ash, grey ; 97 p. c.		Sp. gr. of coal 1·329. Ash, grey ; 9·88 p. c.		Sp. gr. of coal 1·340 Ash, greyish-white; 9·68 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alumina.....	22·91	14·55	21·13	14·21	20·24	16·02
Ferric oxide.....	1·55	trace	1·39	—	1·42	—
Lime.....	0·81	—	0·78	trace	0·74	—
Magnesia.....	trace	1·05	0·61	—	0·57	—
Sulphuric oxide.....	0·17	—	0·16	—	0·11	—
Phosphoric „.....	0·59	—	0·55	—	0·64	—
Silica.....	—	58·25	—	61·02	—	60·21
Undetermined and loss..	0·12		0·16		0·05	
	26·03	73·85	24·61	75·23	23·72	76·23
	100		100		100	

The ashes of these coals show a notable increase in the percentage of silica, as compared with those of the other fields, and a much lower percentage of soluble to insoluble alumina, the ratios, taking the insoluble as 1, as before, being—

Vale of Clwydd.	Eskbank.	Lithgow.
1 : 1·5	1 : 1·4	1 : 1·2

The phosphoric oxide is intermediate in quantity between that of the Hunter River and Southern coals, but if the additional quantity of ash be supposed to be introduced from extraneous sources, the proportion of phosphoric oxide will approach more nearly to the former.

Torbanite or *Kerosene Mineral*.—This mineral, of which New South Wales possesses deposits of incomparable excellence at Joadja Creek, near Berrima, Hartley, and elsewhere, yields between 70 and 80 per cent. of volatile hydrocarbons, and is successfully used for the production both of gas and of illuminating oils and paraffins. The seam at Joadja Creek is covered by a thin stratum of bituminous coking coal, whilst beneath there is a similar layer of inferior quality, the true floor and roof being of sandstone rocks. The following are analyses of the ash of each division of the seam:—

	Top Coal.		Torbanite.		Bottom Coal.	
	—		Sp. gr. 1·098. Ash, greyish-white; 10·27 p. c.		— Ash, grey; very dense; 22·88 p. c.	
	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.	Sol. in acid.	Insol. in acid.
Alkalis and chlorine (sol. in water).....	4·05	—	—	—	0·85	—
Alumina	11·23	22·15	14·74	5·40	20·04	7·79
Ferric oxide	11·55	trace	0·76	trace	1·84	trace
Lime	0·20	—	0·30	—	0·28	—
Magnesia.....	0·63	—	0·45	—	0·36	—
Phosphoric oxide.....	0·92	—	0·65	—	0·44	—
Silica	—	48·66	—	77·12	—	68·63
Undetermined and loss..	0·41		0·58		—	—
	28·58	71·01	16·90	82·52	23·81	76·42
	100		100		100·23	

The ratios of insoluble to soluble alumina in these ashes are :—

Top coal.	Torbanite.	Bottom coal.
1 : 0·5	1 : 2·7	1·25

It is remarkable that a large percentage of ferric oxide is required to give a decided colour to coal-ashes, and it appears impossible to judge by appearance of the quantity actually present. Thus some of the Newcastle coals with 9 per cent. or a little over, are decidedly red, whilst the Joadja Creek coal containing 11 per cent., has only a faint pink colour. F. Muck observes (*Zeitschr. Anal. Chem.*, **19**, 131) that coal-ashes rich in lime are but slightly coloured even by a large proportion of ferric oxide, and he ascribes this result to the presence of the iron in the form of calcio-ferric silicate. The ashes of the New South Wales coals contain but little lime, and yet the iron does not communicate to them nearly the same colour that it does to other earthy substances, brick-dust for example, which has a decided red colour if it contains 10 per cent. ferric oxide. H. W.

Graphite from Ducktown, Tennessee. By W. L. DUDLEY and F. W. CLARKE (*Amer. Chem. J.*, **2**, 331).—A large mass of mineral from this locality was found to consist of graphite mixed with copper pyrites and various silicates. The purest specimen obtainable yielded 67·90 per cent. carbon, and 12·01 ash, having the following composition :—

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	CuO, Mn ₂ O ₃ .
41·06	26·69	20·37	9·76	2·04	traces = 99·92
3 x 2					

This is nearly an impure iron epidote, the oxygen ratios being
 $RO : 2R_2O_3 : 3SiO_2$.
 H. W.

Miscellaneous Contributions to Microscopical Mineralogy.

By H. FISCHER (*Jahrb. f. Min.*, 1881; 2 Ref. pp. 17—21).—These communications are a continuation of the author's "Critical Studies," and deal partly with the proofs of the homogeneous nature of opaque substances, and partly with the crystal system of microcrystalline minerals.

SULPHUR COMPOUNDS.—*Berthierite*.—Sections of this mineral from Brünnsdorf and Arany Idka (Hungary), were found to contain small cubes of pyrites, and although that from Andreasberg contains no pyrites, yet it contains small needles with a brass-like tarnish. These enclosures explain the varying fusibility and composition of this mineral, of which three different varieties are supposed to exist. Opaque bodies can often be examined by acting on a polished surface with nitric acid, as is done with meteorites. The remark is here made that chrome-iron ore is often penetrated by a colourless, transparent, anisotropic body in considerable quantity, and consequently it is not justifiable without further proof to consider the magnesia and alumina as belonging to the chrome-iron ore itself.

Schaalenblende from Geroldseck near Lahr is Wurtzite.

SILICATES.—*Bowlingite*, from Scotland, first described by Hannay, and said to be a silicate of alumina, magnesia, and iron, combined with 4.98 per cent. calcium carbonate; but no section of this new species was examined by him, which was an absolute necessity. *Klipsteinite* from Herborn in Nassau was described by v. Kobell as a hydrated silicate of magnesia, alumina, ferric, manganic and manganous oxides, which evolves chlorine when heated with hydrochloric acid. The powder examined microscopically consists of red-brown transparent isotropic particles, opaque black particles, and very thin lamellæ, which are probably a hydrated manganese oxide. *Carpholite*. The needles are faintly dichroic, and the vibration directions are parallel or inclined to the length of the crystals, according as they lie. No trustworthy optical data could be determined with *Crocodylite*. *Slag-like augite* from Giuliana in Sicily, consists of layers of black augite and quartz; it is reported to occur in limestone, but judging from this specimen trachyte would be a more likely matrix. *Beauxite* is a mixture of ferric oxide and red-clay. From *Isopyr* no transparent section could be obtained, but the powder was translucent, brown, and isotropic, i.e., it is amorphous. *Aphrodite* is lamellar and homogeneous, but no optical data could be determined. *Stilpnomelane*. The outlines of the thin plates are too indistinct to compare with the depolarising directions. Small reddish-yellow mica plates coated with fibrolite occur in a mica-slate from Freiburg (Baden); these the author has previously shown to be the constituents of *anthosiderite*, but it is nevertheless still reckoned as a distinct species. A crystal of *Lapis-lazuli* was seen to consist of blue and of white portions, neither of which are however homogeneous. *Blue sodalite*, *Jadeite*, from China, is probably monosymmetrical, as the depolarisation directions are inclined

to the fibres, formerly only known in the form of ancient axe heads. The oxygen ratios $\text{RO} : \text{R}_2\text{O}_3 : \text{SiO}_2$ vary; 1 : 2 : 6, 1 : 2 : 5, 1 : 2 : 7, 1 : 3 : 8; $\text{Cr} = 3\cdot2\text{--}3\cdot4$; $\text{H} = 7$. *Chlormelanite*. Sections of *Fayalite* from the Mourne Mountains showed only a few yellow transparent particles of foreign matter; magnetite could be extracted; specimens from Fayal show inclined depolarisation directions (7°), and so are perhaps not rhombic.

PHOSPHATES.—*Monazite*, from Norway, contains numerous yellow and brown particles (ferric oxide), a flocculent substance amounting sometimes to one-third of the whole, and some American specimens contain numerous coloured needles. *Svanbergite* (Sweden) owes its yellowish-red colour to streaks of enclosed ferric oxide. *Cryptolite*. The needles of this substance lie parallel to each other, and to the axis of the enclosing apatite; the depolarisation directions are not inclined to the length of the prisms; the apatite also encloses ferric oxide scales and brown flocks of an unknown mineral. *Cacoëne* (Bohemia) needles show no dichroism, but inclined depolarisation directions, $5\text{--}8^\circ$.

ARSENATES.—*Arsenosiderite*.—The fibres are only transparent when very thin, and then appear to have parallel depolarisation directions, and to show no dichroism or absorption.

SULPHATES.—*Aluminite* from Halle consists of prisms with angles of $107\text{--}108^\circ$, towards which the depolarisation direction is inclined at 48° ; they are 0.04 mm. long, and 0.004 mm. thick. The needles from Epernay described by Kennigott as Felsöbanyite, do not act on polarised light, and are therefore something different. H. B.

New South Wales Minerals. By A. LIVERSIDGE (*J. Roy. Soc., N.S.W.*, 14, 213—225).—*Alunogen*.—Fibrous masses made up of long acicular crystals, white with silky lustre like satin-spar. Found as an efflorescence in a sandstone cave near Wallerawang; very commonly met with elsewhere in the caves and overhanging ledges of the sandstone rocks of the Colony.

SO_3 .	Al_2O_3 .	H_2O .	K_2O .	Na_2O .	Insol. and loss.
34.685	15.198	47.535	0.337	0.931	1.314 = 100

These numbers agree nearly with the formula $\text{Al}_2\text{O}_3, 3\text{SO}_3 + 18\text{H}_2\text{O}$. Another specimen from the same place was found to contain a considerable quantity of magnesium sulphate (36.8 per cent. MgSO_4).

Andradite (common garnet).—Associated with magnetite at Wallerawang; brown, rather dull. Crystallised in rhombic dodecahedrons.

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .	K_2O .
34.164	3.251	29.435	0.931	0.553	28.303	0.341
Na_2O .	CO_2 .	H_2O .				
0.186	1.982	0.322	= 99.468			

Atacamite.—Crystallised in radiate groups of small acicular crystals. Dark olive-green with vitreous lustre, apple-green streak. Translucent. New South Wales, but exact locality unknown.

CuO.	CuCl ₂ .	SiO ₂ and insol.	H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾
64.709	13.218	7.599	13.955	0.536 = 100.017

¹ Combined.² Lost at 105°.

Bismuthite.—Dull grey or white earthy-looking rolled fragments, usually about the size of a pea, but sometimes in larger pieces. Fracture dull earthy. H. = 3 to 4. From Pond's Creek; found also, with stream tin, over most parts of the New England tin district.

SiO ₂ .	Bi ₂ O ₃ .	Al ₂ O ₃ and Fe ₂ O ₃ .	CO ₂ .	H ₂ O.
4.695	76.061	1.983	5.426	11.835 = 100

These numbers do not agree with the usual formula of bismuthite, the specimen being contaminated with silica, alumina, &c.

Cacholong.—Opaque, porcelain-white, passing into white opal. Adheres strongly to the tongue. H. = 5 to 6. Sp. gr. 1.884. From the Tumut river.

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾
88.811	1.206	1.134	0.485	5.185	2.553 = 99.374

¹ Combined.² Given off at 105°.

Chloropal.—In veins in the basalt at Two-mile Flat, near Mudgee. Pistachio-green, and yields a green powder. Somewhat fibrous in parts; looks like a decomposition-product. Friable. Fracture splintery to earthy. H. = 2.3. Sp. gr. = 1.94. Smells like clay when breathed on. Before the blowpipe it blackens, does not fuse, becomes magnetic. Hydrochloric acid decomposes it, with separation of silica.

SiO ₂ .	Fe ₂ O ₃ .	Mn.	CaO.	MgO.	Na ₂ O.	K ₂ O.
49.657	29.108	trace	2.606	0.508	0.599	0.170

H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾
5.224	12.313 = 100.185

Combined.

² At 105°.

Copper.—Diffused grains of metallic copper occur in a dark-grey porphyritic phonolite near Kiama.

Chrysocolla.—From Whecco. Massive. Bluish-green, much darker outside than within. Fracture somewhat splintery and conchoidal. H. = 4. Sp. gr. 2.37 to 2.43.

SiO ₂ .	CaO.	Iron oxide.	H ₂ O (comb.).	H ₂ O (at 120°).
43.11	35.28	trace	9.40	11.92 = 99.71

These numbers do not answer to the usual formula. Probably some of the silica exists in the free state.

Grossularite (Lime-alumina Garnet).—From near Mudgee. Of a rich dark-brown colour. Translucent. Imperfectly crystallised in groups of large rhombic dodecahedrons.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	CO ₂ .
40.517	19.906	0.285	3.165	3.700	32.245	traces	0.254 = 100.072

Halloysite.—Black; brittle. Fracture conchoidal. Makes a black streak on paper. Somewhat greasy to the touch; does not adhere to the tongue. Soft, readily scratched by the nail, leaving a shining streak. Found near Berrima.

SiO ₂ .	Al ₂ O ₃ .	CaO.	H ₂ O (comb.).	H ₂ O (at 105°).	
45·289	38·547	trace	12·840	3·047	= 99·723

Hematite.—Very common on the Hawkesbury sandstone. Gives a red streak. Sp. gr. 4·49. From the neighbourhood of Sydney.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO, CaO, MgO.	H ₂ O (at 105°).	
4·210	0·713	90·555	3·632	traces	0·646	= 99·756

A very good iron ore, though often mixed with sand and other impurities.

Brown Hematite.—(1). From the neighbourhood of Jamberoo. Massive, somewhat vesicular in plates. Colour dark brown to pitch-black. Streak brown. Sp. gr. 3·52. (2). Found with the titaniferous iron ore of Uralla. Massive. Sp. gr. 3·611.

	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Al ₂ O ₃ .	SiO ₂ .
(1.)	77·155	—	0·428	0·257	trace	1·232	8·507
(2.)	77·132	3·526	0·940	2·022	trace	0·159	3·782

H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾	
11·872	1·335	= 100·786
10·652 ³	1·787 ⁴	= 100

¹ Combined. ² Lost at 105°. ³ Combined (by diff.). ⁴ Lost at 100°.

Limonite or *Clay-band Iron Ore*.—(1) From Wallerawang; taken from the outcrop of a seam, and probably altered by the action of bush-fires, since the proportion of water is much below the calculated amount; moreover, the mineral contains a trace of magnetic iron, and yields a powder of dark chocolate instead of the usual yellow colour; (2) and (3) Wallerawang; (4) Jamberoo; dark reddish-brown, with the aspect of a clay or shale, which in fact it is. Structure somewhat laminated. Fracture flat conchoidal, with dull earthy surface. Sp. gr. 2·73. (5.) *Limonite concretions*. Small nodules, of spherical or elongated shape, some having a wrinkled or corrugated surface. Structure concentric, occasionally radio-fibrous in the outer portions. Sp. gr. 3·52. H. 3—4. Streak or powder yellow.

	1.	2.	3.	4.	5.
Fe ₂ O ₃	85·32	78·96	77·29	13·02	81·78
FeO	0·52	0·67	0·46	1·26	—
MnO	1·60	2·43	0·76	0·26	0·56
CaO	0·35	0·65	0·19	0·16	0·50
MgO	0·29	0·14	0·28	trace	trace
Al ₂ O ₃	2·13	1·38	1·20	15·07	0·63
SiO ₂ (insol.)	3·63	3·66	8·34	57·26	5·82
„ (sol.)	0·51	0·07	0·27	—	—
P ₂ O ₅	trace	trace	trace	trace	—
S	0·04	trace	trace	—	—
H ₂ O (combined)	4·17	10·29	10·07	11·00	7·30
„ (hygroscopic) ..	1·31	1·35	0·97	1·45	3·17
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	99·87	99·60	99·83	99·48	99·76
Metallic iron per cent. in Fe ₂ O ₃ and FeO ..	60·13	55·80	55·46	—	—

Magnetite.—From a vein at Wallerawang, where it is associated with a vein-stuff composed of a ferruginous garnet. The magnetic and non-magnetic portions were separated by a magnet and analysed; but it was found impossible to obtain the magnetite quite free from the vein-stuff. (a.) Magnetic. (b.) Non-magnetic.

	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Al ₂ O ₃ .	SiO ₂ .	CO ₂ .
(a.)	70·47	6·91	2·39	6·96	0·20	1·97	9·26	—
(b.)	35·91	0·56	1·62	24·44	1·00	1·13	32·54	1·66

	Zn,Ni.	H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾
(a.)	0·13	1·69	0·26 = 100·24
(b.)	—	1·14	0·21 = 100·21

¹ Combined.

² Given off at 100°.

Of the silica, 0·65 in the magnetic, and 3·88 in the non-magnetic portion, is of the soluble modification. The magnetic portion contains also traces of sulphur and phosphoric oxide.

The non-magnetic portion answers to the general formula of iron-lime garnet, 3CaO, 2SiO₂ + Fe₂O₃, SiO₂.

Hausmannite?—A hard compact mineral, with a very minute crystalline structure; found in the Wellington district. Strikes fire with steel. Fracture conchoidal. Colour dark iron-grey. Sp. gr. 6·466. H. = 6·5. Dissolves in strong hydrochloric acid, eliminating chlorine and leaving a white residue.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	MnO ₂ .	CaO,MgO.
11·78	4·06	3·15	31·52	50·12	traces = 100·63

Menaccanite.—A variety of titaniferous iron found in the river deposits near Uralla, in the form of black pebbles, with submetallic lustre. Sp. gr. 4·44.

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe.	O.	CaO,MgO.
9·49	44·51	14·80	23·02	8·18	traces = 100

The iron exists both as ferrous and as ferric oxide, the former predominating; but as it is not easy to estimate accurately the proportion of ferrous oxide in a difficultly soluble mineral like this, the total iron has been stated as metallic iron, and the oxygen estimated by difference.

Pyroxene.—From Oberon. Green; more or less decomposed, retaining only traces of previous crystallisation. Soft and fragile. Sp. gr. 3·48.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O (at 100°).	
35·32	5·92	28·56	1·81	4·06	22·75	0·38	0·22	0·21	= 99·23

Scheelite.—From the Victoria Reef Gold Mine, Adelong. Massive, with a portion of a crystal showing on one side, of an amber colour, translucent, with resinous lustre, and splintery fracture; brittle. H. = 4 to 5. Sp. gr. 6·097. It is associated with a dark-green chloritic vein-stuff.

WO ₃ .	CaO.	Al ₂ O ₃ .	MgO.	Loss at red heat.
79·53	19·14	0·58	0·07	0·25 = 99·57

These numbers correspond with the formula CaWO₃.

Siderite or *Ferrous Carbonate*.—Diffused through a compact grey claystone from the neighbourhood of Jamberoo. Sp. gr. = 2·79. The following analysis was made of the whole, as the particles of siderite could not be separated.

CO ₂ .	FeO.	MnO.	MgO.	Al ₂ O ₃ .	SiO ₂ .	TiO ₂ .	H ₂ O. ⁽¹⁾	H ₂ O. ⁽²⁾	
7·82	12·87	1·05	trace	22·84	42·29	0·72	11·92	0·93	= 100·44

¹ Combined.

² Given off at 100°.

Tinstone or *Cassiterite*.—A specimen of almost black stream tinstone from the Jupiter Mine, Vegetable Creek, New England.

SnO ₂ .	TiO ₂ .	Al ₂ O ₃ .	SiO ₂ .	Fe ₂ O ₃ .
89·92	0·69	6·75	0·80	2·30 = 100·46

Wolfram.—Found in quartz veins, with tinstone at Inverell. Bronze-black, with submetallic lustre. Opaque. Structure lamellar, with only traces of crystal faces. Contains 77·64 WO₃, 18·76 FeO, and 4·12 MnO = 100·52.

A pink schistose mineral imbedded in the slates and other rocks at the south-east corner of Rocky Ridge, gave by analysis 61·95 per cent. SiO₂, 24·12 Al₂O₃, 3·40 Fe₂O₃, 1·22 FeO, 7·85 CaO, and 1·33 water (= 99·87): evidently a product of decomposition. H. W.

Mineralogical Notices. By V. V. ZEPHAROVICH (*Zeitschr. f. Kryst. u. Min.*, 5, 96; *Jahrb. f. Min.*, 1881, Ref., 2, 162—166).—*Phillipsite* from *Salesi in Bohemia*.—This mineral occurs in the cavities of a vein of felspathic basalt, in the lignite beds of the above locality, together with analcime, phacolite, and calcite. It exhibits the known faces 0P, ∞P∞, ∞P, together with ∞P∞, —5P∞, and lastly a face in the

zone $\infty P : \infty P\infty$, apparently corresponding with the face $\infty P2$ mentioned by Streng. Axes $a : b : c = 0.6991 : 1 : 1 : 2.124$; $B = 55^\circ 34'$. Three kinds of complex crystals were recognised by external characters, viz., twins according to OP , double twins according to OP and $P\infty$, and a combination of three of these double twins with ∞P as twin-plane.

The *analcime* crystals, which were somewhat furrowed, exhibited the face 202 , and on one crystal $\infty O\infty$ was observed. The *calcite*, yellowish or grey, exhibits $-2R$, or occurs in the spathic form.

There also occurs a very soft greenish-black substance in the form of a thin finely botryoidal crust, sometimes covered with a lighter layer of ash-grey or greenish-blue grey colour, or having a scaly structure from interstratification with the latter. This substance appears to be a decomposition-product of an iron carbonate, and contains, according to qualitative analysis, SiO_2 , Fe_2O_3 , FeO (in small quantity), CaO , MgO , and H_2O , and may perhaps be regarded as chlorophæite, having its ferrous oxide for the most part converted into ferric oxide.

With regard to the paragenesis of these three minerals, the author remarks that, supposing them to have been formed essentially at the same time, the substance resembling chlorophæite always forms the substratum, then follow in order calcite, analcime, phillipsite, and a second formation of calcite.

II. *Ilmenite from the Kapruner-Thörl in the Pinzgau.*—This mineral belongs to the varieties containing a medium amount of titanic oxide, and forms thin layers with irregular surfaces, intergrown with quartz, or freely implanted in its cavities. It is associated with scaly-granular groups of blackish-green chlorite, and with rhombohedral calcite containing small quantities of magnesium and iron, imbedded in the quartz. The calcite is brownish, and shows on its dull faces distinct marks of erosion, some of the individual crystals having been completely dissolved, leaving corresponding cavities. According to Peters, this ilmenite occurs at the boundary of gneiss and mica-slate.

III. *Minerals from the Iron Mine of Morawicza in the Bannat.*—

1. *Metamorphosis of a mineral of the Augite group.*—In a large block of garnet in this mine there was found enclosed a very soft dark brown substance having a red streak, little or no lustre, and a texture like that of many actinolite groups. It contained particles distinguished from the rest of the mass by their superior lustre and hardness, also cavities lined with ill-defined crystals of the same substance, together with small crystals of quartz and garnet and lamellæ of iron-glance. The analysis of the mass did not reveal the existence of any definite chemical compounds, but from the occurrence in it of the minerals just mentioned, and its separation into prismatic portions which may be attributed to its original cleavability, the author infers that it is a transformation-product of fowlerite.

2. *Grammatite* (asbestiform tremolite) from the Eleonora shaft. This mineral forms greenish-white to oil-green groups, having a silky

lustre, and made up of closely packed radiofibrous spheroids. Fine-grained magnetite occurs in the middle of the structure and between the fibres, or crossing them externally. According to Hidegh, the grammatite is composed of 56.93 per cent. SiO_2 , 0.64 Al_2O_3 , 21.73 MgO , 15.12 CaO , 3.87 FeO , 0.37 MnO , and 1.25 matter lost by ignition (total 99.91), whence, neglecting the alumina and the loss by ignition, may be deduced the proportion $\text{SiO}_2 : \text{Mg}(\text{Fe}, \text{Mn})\text{O} : \text{CaO} = 3.51 : 2.23 : 1$ and $\text{SiO}_2 : \text{RO} = 1.09 : 1$. Sp. gr. = 2.987. Thin splinters, melting easily before the blowpipe to a light green blistered glass.

Another occurrence of grammatite "enclosed in very compact magnetite," exhibits similar relations, the greenish-white substance, as in the former case, having but little hardness, and its fibres being more easily separated one from the other than those of the oil-green substance. The author therefore regards the former as a modification resulting from substantial alteration of the latter.

3. *Serpentine from the Jupiter-Tagbau*.—A fibrous green serpentine, having a texture very much like that of the last-described mineral; may be separated from serpentine of a somewhat darker oil-green to finch-green colour. According to an analysis by Hidegh, it contains 42.33 per cent. SiO_2 , 43.08 MgO , 1.88 FeO , and 13.63 H_2O (total 100.92), besides traces of MnO , but no alumina or alkalis. $\text{SiO}_2 : \text{RO} : \text{H}_2\text{O} = 2 : 3 : 12 : 2.14$. Sp. gr. = 2.55.

According to a communication from A. Veszely, this serpentine occurs in bands in a compact garnet. The author thinks it probable that this fibrous serpentine is a far-advanced alteration of grammatite, although the latter does not occur in the Jupiter-Tagbau. Magnetite is also present in this locality, and the examination of thin sections reveals, as accompanying minerals, steatite-scales, calcite, and ludwigite.

4. *Calcite* is also found in large pale bluish-green, pistachio-green, or yellowish-white crystals, with the faces $\text{R}3$ or $-\frac{1}{2}\text{R}$ predominant; also on small peach-blossom-coloured scalenohedrons of later formation.

H. W.

Crystals of Metallic Copper from the Mines of Coro-Coro in Bolivia. By I. DOMEYKO (*Jahrb. f. Min.*, 1881, 2, 178).—These crystals belong to the well-known pseudomorphs of copper after aragonite, which, when they occur in large quantity, exhibit all the phases of transformation of the perfectly pure trilling of aragonite into nearly pure metallic copper. The structure of these Bolivian pseudomorphs, and their occurrence together with unaltered aragonites, in a clay impregnated with solutions of sodium chloride and copper salts, afford, according to the author, the conditions which may determine the separation of copper under the influence of electric currents somewhat in the manner of Becquerel's electro-capillary apparatus.

H. W.

Gallium in American Blendes. By H. B. CORNWALL (*Amer. Chem. J.*, 2, 44).—The compact greyish blende of Friedensville and the yellow-brown blende of Phœnixville, Pa., were found by the

author to contain a comparatively large quantity of gallium. In specimens from Joplin, Ms., Warren, N.H., and Ellenville, N.Y., gallium was recognisable by the spectroscope. H. W.

Fredricite, a Mineral Resembling the Fahl-ore from Falu. By H. SJÖGREN (*Jahrb. f. Min.*, 1881, 2, Ref. 31—32).—This mineral occurs in pieces as large as a walnut in a vein of coarsely crystallised galena, which contains also geocronite. It is most nearly related to arsenical fahl-ore, but differs in its denser form, darker colour, and in containing lead, tin, and silver. It is opaque and iron-black, has a strong metallic lustre, and a fine conchoidal fracture; but evidences of crystallisation are absent; somewhat brittle; streak black; sometimes tarnished. $H. = 3.5$. $Sp. gr. = 4.65$. It decrepitates and then melts easily before the blowpipe. The analysis, which was not conducted in the usual manner, gave:—

Cu.	Fe.	Pb.	Ag.	Sn.	As.	Sb.	S.
42.23	6.02	3.34	2.87	1.41	17.11	trace	27.18 = 100.16

Hence the formula $4(Cu_2, Fe, Pb, Ag_2, Sn)S.As_2S_3$, which agrees exactly with that of arsenical fahl-ore. The only other mineral containing tin, found in Sweden, is tinstone, and this occurs as a great rarity.

H. B.

Bismuth Ores of Bolivia, Peru, and Chili. By I. DOMEYKO (*Annales des Mines* [7], 18, 538; *Jahrb. f. Min.*, 1881, 2, Ref. 158).—Bolivia is, according to the author, the richest of all the countries in bismuth. The ores are usually associated with tinstone, and sometimes with silver and gold. The quantities of bismuth found in Peru and Chili are comparatively small.

The bismuth-ores of Bolivia consist of sulphides, oxides and metallic ores.

1. **SULPHUR-ORES.** *Bolivite*, Bi_2S_3 , Bi_2O_3 , apparently rhombic, found at Tazna.—*Bismuth-glance* occurs chiefly at Chorolque, near Tazna.—*Bismuth-copper sulphide*: from the mines of Cerroblanco in the Chilian province of Atacama.—*Bismuth-silver sulphide*. Found by Pflücker in the Santa Matilda de Morocochu mine in Peru.

2. **OXIDES.** *Taznite*. Chlorarsenate and Chlorantimonate of Bismuth: occurs at the outcrop of the veins.—*Bismuth Hydroxide*. Compact and earthy, the most abundant of the Bolivian bismuth ores.—*Hydrated Bismuth Silicate*: accompanies the bismuth-glance of Chorolque.

3. **METALLIC ORES.** *Native Bismuth*.—Of rather frequent occurrence in Bolivia; found together with oxysulphide at Tazna; contains no tellurium. In other localities it is associated with gold.—Telluric bismuth, and bismuth-silver. H. W.

Calcespar in Basalt-tufa from Owener Bölle. By LEUZE (*Jahrb. f. Min.*, 1881, 2, Ref. 23—24).—In the basalt-tufa of a hill—the so-called Bölle—in the neighbourhood of Owen, near Kirchheim and Teck in Würtemberg, calcespar crystals occur in considerable numbers, besides zeolites and other minerals, in all the clefts and

hollows in the rock. These crystals are very perfect and as clear as Iceland spar, and are interesting through the occurrence of + R and - R and numerous faces. They are often covered by a second crystallisation with an acute rhombohedral type. The author describes the crystallographical examination of the older crystals. + R sometimes occurs alone, and only then with smooth lustrous faces. - R generally occurs with + R, the two forming a hexagonal pyramid; the - R faces are always lustrous. ∞ R and ∞ P2 are always short. $-\frac{1}{2}$ R is sometimes rather rounded. - 2R and $\frac{2}{3}$ P2 occur frequently. Zippe observed this only as a rarity on crystals from Montecchio, Maggiore. In some cases all these forms occur together. H. B.

Sample of Diadochite from the Védurin Mine. By F. DEWALQUE (*Jahrb. f. Min.*, 1881, 2, Ref. 30).—In appearance like the earthy variety described above, but consists of crystalline needles 0.005—0.01 mm. long, which appear to be monosymmetrical, judging by their action on plane polarised light. Sp. gr. = 2.27. It gave on analysis:—

Al ₂ O ₃ .	FeO ₃ .	P ₂ O ₅ .	As ₂ O ₅ .	SO ₃ .	H ₂ O.	CaO.	Insoluble residue.
0.8	39.8	15.9	trace	13.9	28.7	trace	0.9 = 100.0

H. B.

Two Varieties of Diadochite (Phosphato-sulphate of Iron) found in the Coal Mine at Psychagnard (Isère). By A. CARNOT (*Jahrb. f. Min.*, 1881, 2, Ref. 29—30).—The two varieties often occur on the same specimen; one is bright brown and semi-transparent, with a conchoidal fracture and glassy lustre; the other is yellowish-white, perfectly opaque, has an earthy fracture and is dull; other specimens are intermediate in appearance; the sp. gr. varies from 2.22 to 2.10; both forms are quite amorphous, and are easily rubbed to powder between the fingers. Analyses of the brown (1) and of the yellow (2) varieties are given, also the (3) analysis of a sample from Huelgoat by Berthier; the formula $2(\text{Fe}_2\text{P}_2\text{O}_8) + \text{Fe}_4\text{S}_3\text{O}_{15} + 30\text{H}_2\text{O}$ requires the percentages given in No. 4.

	Fe ₂ O ₃ .	P ₂ O ₅ .	As ₂ O ₅ .	Sb ₂ O ₅ .	SO ₃ .	H ₂ O.
(1.)	36.63	16.70	0.45	—	13.37	32.43
(2.)	36.60	17.17	—	—	13.65	32.20
(3.)	38.5	17.0	—	0.5	13.8	30.2 (by diff.)
(4.)	37.56	16.67	—	—	14.08	31.69

	CaO.	MgO.	Organic substances.	
(1.)	0.30	trace	—	= 99.88
(2.)	0.15	trace	trace	= 99.77
(3.)	—	—	—	= 100.00
(4.)	—	—	—	= 100.00

Dufrénoy remarks that the formation of this mineral at Huelgoat depends on the pyrites and lead phosphate occurring there; and Rolland explains its occurrence at Psychagnard by the water filtering through the fossil limestone occurring with the coal, and so taking up ferrous oxide, sulphuric acid, and phosphoric acid. H. B.

Artificial Production of Vivianite. By J. GIRARDON (*J. Pharm.* [5], 4, 14—16).—"Spent" bone-black (that which has been used for decolorising sugar solutions) when ignited leaves a semi-fused mass of a colour varying from that of verdigris to that of ultramarine, due to the formation of *vivianite*. The iron, which originally is not found in the bone-black, is introduced during the manufacture by the action of the more or less acid beetroot juice on the iron of the vessel, and the iron salt thus formed is retained in the pores of the charcoal.

Vivianite has also been obtained by fusing a salt of iron with bone-black.
L. T. O'S.

Thaumasite and Melanophlogite. By E. BERTRAND; and **Remarks on Thaumasite.** By A. E. NORDENSKIÖLD (*Jahrb. f. Min.*, 1881, 2, Ref. 21—22).—In a section of thaumasite (*Jahrb. f. Min.*, 1880, Ref. 37) Bertrand found calcite, gypsum, and a third mineral, probably wollastonite, verifying the optical behaviour of the first two; and according to experiments of Damour this mineral is only a mixture of the above three. To these results Nordenskiöld replied that a mineral with 42·2 per cent. water, and a sp. gr. of 1·877 cannot be a mixture of these three other minerals, whose specific gravities lie between 2·32 and 2·8, and two of which are anhydrous, whilst the third contains only 20·9 per cent. water. It can hardly be supposed that the calcium silicate exists as $\text{CaSiO}_3 + 12\text{H}_2\text{O}$, which would contain 65 per cent. water. The specimens were obtained in 1802—1805, 1859, and 1878, were perfectly homogeneous, and had identical composition. E. Cohen has also examined a specimen and found it to be a homogeneous fibrous mass, not capable of optical examination, but by treatment with dilute acetic acid numerous needles with inclined depolarisation directions were obtained; a few plates of gypsum were found, but the presence of these and of the carbonates soluble in dilute acetic acid in this specimen, are by no means sufficient proof of the non-existence of thaumasite.

Bertrand has shown by optical examination that the apparent cubes of melanophlogite consist of six pyramids whose apexes are in the centre of the crystal, and whose basal faces form the six faces of the cube.
H. B.

Composition of Descloizite and the Natural Vanadium Compounds in General. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1881, 2, Ref. 26—28).—The author has obtained a rich lot of vanadates from the Argentine Republic. *Descloizite*.—Damour, who made the first analysis of this mineral, considered the contained Mn, Fe, Zn, Cu and water as mere mechanical mixtures, and accordingly gave it the formula $\text{Pb}_2\text{V}_2\text{O}_7$. Also Tschermak's formula PbV_2O_6 for descloizite is not certain, on account of the incorrect method of analysis; and further, Frenzel's descloizite from Wanlock Head is another vanadate. Rammelsberg analysed dark (A) and light-brown (B) crystals.

	Cl.	V_2O_5 .	PbO.	ZnO.	MnO.	H_2O .	Sp. gr.
A ..	0·24	22·74	56·48	16·60	1·16	2·34 =	99·56 6·080
B ..	—	—	54·35	20·93	—	—	5·915

Whence $R : V : H_2O = 1.9 : 1 : 0.5$ and the formula $R_4V_2O_9 + Aq.$ In the lighter varieties equivalent quantities of Zn and Pb are present; the darker contain some manganese replacing the zinc.

Vanadinite.—In small brown (A) or yellow prisms (B).

	Cl.	V_2O_5 .	P_2O_5 .	PbO.	ZnO with a little Mn.	Sp. gr. (containing quartz).
A ..	—	21.32	76.96	0.80 =	—	6.635
	2.36	18.40	0.76	76.73	0.94 =	
B ..	2.19	20.88	1.05	74.22	2.48 =	100.82
						6.373

The author then critically considers the other vanadates. The complete list being—

(1.) Simple vanadate, $R''V_2O_6$. Dechenite, PbV_2O_6 (?).

(2.) Half vanadate, $R''_2V_2O_7$. Lead vanadate from* Wicklow according to Thomson, and from Wanlock Head according to Frenzel, $Pb_2V_2O_7$ (?).

(3.) Third vanadates, $R''V_2O_8$.

(a.) Eusynchite $(Pb,Zn)_3V_2O_8$.

(b.) Aräoxen $(Pb,Zn)_3(V,As)_2O_8$.

(c.) Vanadinite, $PbCl_2 + 3(Pb_3V_2O_8)$.

(d.) Pucherite $(Bi_2V_2O_8)$.

(4.) Quarter vanadates, $R''_4V_2O_9$.

(a.) Descloizite $(Pb,Zn)_4V_2O_9 + Aq.$

(b.) Volborthite $(Cu,Ca)_4V_2O_9 + Aq.$

The composition of the following is uncertain:—

Psittacinite $(Pb,Cu)_9V_4O_{19} + 9Aq.$ See Genth, *Am. Journ. Soc.* [3], 12, 35.

Mottramite $(Cu,Pb,Ca)_6V_2O_{11} + 2Aq.$

Volborthite from Perm, $R''_8V_2O_{13} + 24Aq.$; $R =$

$Cu, Ca, Ba, Mg.$

H. B.

Crystalline Form of Descloizite. By WEBSKY (*Jahrb. f. Min.*, 1881, 2. Ref. 24—25). The specimens examined are from the Argentine Republic. These lead vanadates occur in a vein with quartz and brown ironstone, and are the alteration-products of galena; they occur in thin scales and in crystals of $\frac{1}{2}$ to 1 mm. in size. The vanadinite is always of a pale leather-yellow colour, and the descloizite varies from hyacinth-red to a deep brown and black. Massive vanadinite occurs as pseudomorphs after anglesite. No cleavage has yet been detected in descloizite crystals; some of these crystals have a lamellar structure, giving rise to a metallic pearly glance, the faces appearing as if gilt.

Descloizeaux considered this mineral as rhombic, but Websky places it in the monosymmetrical system with an angle β of $89^\circ 26'$ and $a : b : c = 0.6480 : 1 : 0.8023$, retaining as primary prism that of Descloizeaux, but making the $\frac{1}{2}P$ equal to $+P$ and $-P$; furthermore he supposes that most of the crystals are twins, the twin axis being the normal to the basal plane. Numerous forms were measured, and the results compared with those of other authors, and also with the forms of some allied minerals.

H. B.

Crystalline Form of Vanadinite from Cordoba. By WEBSKY (*Jahrb. f. Min.*, 1881, 2, Ref. 25–26).—These pale yellow crystals occur with descloizite, as above described. Generally only ∞P , P , and OP are present, more rarely $2P2$ and a pyramidal hemihedral form. It is interesting that some small thick prisms 1–2 mm. long showed this pyramid of the third order $3P\frac{3}{2}$ largely predominating, and also the faces of $\infty P2$. The angular measurements agreed with those calculated from Urba's numbers, $a : c = 1 : 0.7122$. H. B.

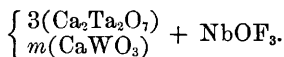
Microlite from Amelia Co., Virginia. By F. P. DUNNINGTON (*Chem. News*, 44, 44).—This mineral occurs with others imbedded in a vein of a "gigantic granite" enclosed in gneiss and mica schist, with the general characters of the Montalbau series. Schorl is very abundant in the adjoining wall-rock. It is found in single crystals, varying in dimensions from one-tenth to three-quarters of an inch, and in larger crystalline masses, of which one was obtained weighing eight pounds. It occurs crystallised in octohedra of the isometric system. The hardness is a little less than 6; sp. gr. 5.656; lustre, glistening resinous; colour, wax-yellow to brown; streak, pale ochreous yellow, subtranslucent; fracture, conchoidal and very brittle. Analysis gave the following results:—

Ta ₂ O ₅ .	Nb ₂ O ₅ .	WO ₃ .	SnO ₂	CaO.	MgO.	BeO.	U ₂ O ₃ .
68.43	7.74	0.30	1.05	11.80	1.01	0.34	1.59
Y ₂ O ₃ .	Ce ₂ O ₃ Di ₂ O ₃ .		Al ₂ O ₃ .	Fe ₂ O ₃ .	Na ₂ O.	K ₂ O.	F.
0.23	0.17		0.13	0.29	2.86	0.29	2.85
							1.17

Considering the bases as replacing equivalent amounts of calcium and neglecting the water, we have the following atomic relations:—

Ca.	Ta.	Nb.	Sn and W.	F.	O.
32.9	30.9	5.8	0.83	15	118.6

If we exclude the Fe₂O₃ and Al₂O₃ as uncombined, as they most probably are, the following formula may be deduced:—



From the results of the above analysis and also from its crystalline habit, it appears that this mineral is the one described by C. U. Shepard as microlite, although it has a composition different from that originally proposed by him, and corresponding with that suggested by Bush, viz., essentially a calcium tantalate. D. B.

Perowskite of Val Malenco. By J. STRÜVER (*R. Accad. dei Lincei* [3], 4; Transunti, *Jahrb. f. Min.*, 1881, 2, Ref. 166).—The yellow octohedral crystals examined were from Monte Lagazzalo in the Val Malenco in the Valtelline, where they occur together with garnet-octohedral crystals of magnetite. They are imperfectly developed, measurable only with the application-goniometer, from 29 to 13 mm. in size, and are very slightly truncated on the edges and summits.

Fracture conchoidal; cleavage very indistinct, parallel to the cube-faces; $H = 5.5$. Sp. gr. = 3.95. Colour, honey-yellow to black. Streak light greyish: lustre of the yellow variety, fatty to adamantine; of the black, adamantine to metallic. The crystals, like all other perowskites, are double-refracting, but are too opaque to admit of exact determination of their optical properties. The substance is infusible, reacts before the blowpipe like other perowskites, and is not attacked by acids, but may be completely disintegrated and rendered soluble in water by fusion with acid potassium sulphate. Gives by analysis 35.77 per cent. titanium, 29.61 calcium (with trace of iron), and 34.75 oxygen, the formula CaTiO_3 requiring 36.23 Ti, 28.99 Ca, and 34.78 O. This perowskite is the first that has been found in Italy. H. W.

On Flint. By L. RICCIARDI (*Gazzetta*, 1881, 319).—Amongst a number of flints collected by the author in the calcareous soil of Vizzini, was one of ovoid shape, and weighing 0.165 gram, the outer layer of which, about a centimeter thick, consisted of a white amorphous substance, whilst the interior exhibited all the characters of true flint. The unaltered part is opaque and of a wax-yellow colour, spotted with white. In the flame of a gas blowpipe it decrepitates like common salt, giving off water, and losing its natural colour. The white altered part also decrepitates, but less strongly. Analysis gave the following results:—

	SiO_2 .	Al_2O_3 .	FeO .	CaO .	H_2O .	Sp. gr.
Unaltered..	96.31	0.30	0.25	0.47	2.81 = 100.14	2.572 at 22°.
Altered....	97.02	0.32	3.99*	0.55	1.68 = 102.96	2.520 ,,

The alteration in the outer crust is probably due to the action of heat, inasmuch as some fragments of the unaltered portion when heated gave off water, and turned white; and this view is further supported by the fact that Vizzini is situated in the district of the extinct volcanoes of Val di Noto. H. W.

Zoïsite. By TSCHERMAK and SIPÖCZ (*Jahrb. f. Min.*, 1881, 2, Ref. 159—162).—The authors have made a series of crystallographic observations on transparent pale-green shining zoïsite crystals from the mines of Ducktown in Tennessee. The crystals belong to the rhombic system. Observed faces $\infty P\infty$, $\infty P\bar{3}$, $\infty P\bar{2}$, ∞P , $\infty P\bar{2}$, $\infty P\bar{3}$, $\infty P\bar{4}$, $\infty P\infty$, $2P\infty$, $P\infty$, P , $2P\bar{2}$. The most fully developed faces are ∞P , $\infty P\infty$, $\infty P\bar{3}$, and P . Cleavage most distinct parallel to $\infty P\infty$; very indistinct parallel to $\infty P\infty$. The angular measurements lead to the axial ratio $a : b : c = 0.61963 : 1 : 0.34925$.

The optical characters are very remarkable. Plates parallel to the macropinacoid exhibit in Nörremberg's polarising apparatus a more or less distorted interference figure, positive if only slightly distorted. The median line is perpendicular to the macropinacoid. The apparent axial angle is greater than 90° , and the dispersion $\rho < v$. In some parts of the crystal the plane of the optic axes is parallel, in other parts perpendicular, to the brachypinacoid. The irregularities may be explained on the supposition of interposed twin-lamellæ, having

* ? 0.39.

the axis a in common with the principal individual, whilst the b -axes of the two are nearly at right angles to each other. According to this, the twin-face would be a face of the dome $3P\infty$, inclined to the axes b and c at the angles $44^{\circ} 49'$ and $44^{\circ} 11'$.

The crystals themselves do not exhibit any signs of twin-connection, but an examination of thin plates in polarised light shows that they are built up of a number of individuals which have their directions of extinction almost exactly parallel to each other, but in other respects are different in optical orientation. The twins appear to be built up in such a manner that the individuals are symmetrically situated with respect to the dome-face $3P\infty$, but are intergrown, not by this, but by the face ∞P . Probably also a second law holds good, according to which the twin-lamellæ are inserted according to $\frac{2}{3}P\infty$.

A crystal of zoisite from Pregratten in Tyrol was found to agree perfectly with that just described in the measurement of the angles; but the plane of the optic axes appeared for the most part parallel to $\infty P\infty$, frequently, however, parallel to $0P$. According to older observations by Miller, Des Cloizeaux, and Brögger, the crystals of zoisite likewise exhibit the faces $4P\infty$, $3P\frac{2}{3}$, $6P\frac{2}{3}$, $\infty P\frac{2}{3}$, $6P\infty$.

The analysis of zoisite from Ducktown gave—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.
39.61	32.89	0.91	0.71	0.14	24.50	2.12 = 100.88

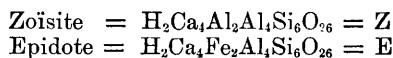
leading to the formula $H_2Ca_4Al_6Si_6O_{26}$.

Tyrolese zoisite, which, however, is not so pure as the American, gave, as the mean of several analyses—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.
39.75	31.45	0.85	1.83	0.13	24.05	2.61 = 100.67

The comparison of older analyses with the numbers calculated from the formula above given exhibits an agreement as near as can be expected in the analysis of silicates.

Comparison of Zoisite with Epidote.—These two minerals differ from one another in their primary forms and in their optical characters, but exhibit a certain similarity in some of their angles. Moreover, zoisite has but one direction of cleavage, whereas epidote has two. Chemically the two minerals resemble one another very closely, excepting that typical zoisite is an alumina compound, whereas in epidote the alumina is partly replaced by ferric oxide; thus—



Natural zoisite and epidote are, inasmuch as the amounts of iron in the two are variable, isomorphous mixtures of Z and E . The mixtures included within the limits Z and Z_2E crystallise rhombic, whereas those between Z_2E and E are monoclinic. The two silicates Z and E are therefore isodimorphous. Zoisite from Ducktown appears to be $Z_{1.5}E$, whereas epidote from Untensalzbach $= ZE_6$. H. W.

Composition of Pollucite from Elba. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1881, 2, Ref. 176).—New analyses of this mineral yielded the following results—(I, II, III); the numbers formerly obtained by the author are given under IV—

	I.	II.	III.	IV.
SiO ₂	46·48	—	—	—
Al ₂ O ₃	—	17·24	—	16·31
Cs ₂ O	—	30·71	30·53	30·00
K ₂ O	—	0·78	0·41	0·47
Na ₂ O	—	2·31	2·19	2·48
Loss by ignition	2·34	—	—	2·59

The water is given off only at a red heat. The formula of the mineral is R₄AlSi₅O₁₅. Sp. gr. = 2·885 to 2·897. H. W.

Sillimanite in the Gneiss of the Morvan. By A. MICHEL-LEVY (*Bull. Soc. Min. de la France*, 3, 1880, 30; *Jahrb. f. Min.*, 1881, 2, Ref. 171).—In the gneiss between the Park of Mont-jeu and Marmagne (Saône-et-Loire), also in the neighbourhood of Mont Saint Vincent, and in that of Cantal (Auvergne), there is very frequently found a white, nacreous, finely cauliform mineral, which by microscopic examination is resolved into a number of very thin prisms (0·01 mm.), vertically striated, and exhibiting in polarised light the characters of the rhombic system. The crystals cleave parallel to the base. The white powder scratches glass, and is indifferent to acids. Sp. gr. 3·2. Analysis gave on the average 42 per cent. silica and 58 alumina: hence the mineral is sillimanite. It occurs in the rock either in irregular clusters, or imbedded parallel to the strata, and always in the neighbourhood of granite-veins which traverse the gneiss. The author compares this sillimanite with a silicate which Deville obtained by the action of aluminium fluoride on silica at a red heat, and directs attention to the fluorine minerals, tourmaline, and white mica, which occur so frequently as enclosures in these rocks. H. W.

Spodumene and its Alterations: from the Granite-veins of Hampshire County, Massachusetts. By A. A. JULIEN (*Amer. J. Sci.* [3], 19, 237).—The investigations relate chiefly to the minerals found at Goshen and at Chesterfield, Mass. Analyses of spodumene as pure and fresh as could be obtained from Levi Barrus Farm, Goshen (I) and from Chesterfield Hollow (II) yielded—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	MgO.	CaO.	Li ₂ O.
I.	63·27	23·73	1·17	0·64	2·02	0·11	6·89
II.	61·86	23·43	2·73	1·04	1·55	0·79	6·99
	Na ₂ O.	K ₂ O.	H ₂ O.				
I.	0·99	1·45	0·36	=	100·63		
II.	0·50	1·33	0·46	=	100·68		

This composition agrees very nearly with the formula given for spodumene by Doelter (*Jahrb. f. Min.*, 1879, 603), viz., Li₂Al₂Si₄O₁₂.

Most spodumenes from the above-mentioned localities are, however,

not fresh, but have been converted into cymatolite. The white crystals thus metamorphosed are of extraordinary size (up to 35 inches long and 11 inches broad) and exhibit a laminated structure. Hardness 1·5 to 2. Sp. gr. 2·69—2·75.

The smaller pseudomorphs from Chesterfield sometimes enclose a blackish-green nucleus of killinite, the larger ones a nucleus of spodumene frequently coated with killinite. Analysis:—I. From the Manning Farm, Goshen. II. From the Barrus Farm (formerly designated by Shepard as *aglaite*). III. From Chesterfield Hollow:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	MgO.	CaO.	Li ₂ O.
I.	58·51	21·80	0·85	0·29	1·44	0·84	0·19
II.	58·11	24·38	1·66	0·18	0·75	0·48	0·09
III.	58·58	22·28	1·77	0·15	0·45	0·93	0·10

	Na ₂ O.	K ₂ O.	H ₂ O.	Org. matter.	
I.	6·88	6·68	2·40	0·44	= 100·32
II.	2·57	8·38	3·01	0·43	= 100·04
III.	9·08	4·48	2·08	—	= 99·90

These numbers lead to the formula $(\text{H}, \text{Na}, \text{K})_6 \text{Al}_6 \text{Si}_{12} \text{O}_{36} + \text{H}_2\text{O}$. The mineral therefore contains 1 mol. water to 3 mols. of a silicate analogous to spodumene.

Killinite occurs less frequently as a pseudomorph after spodumene, the cleavage of the original mineral being still recognisable in its colour, greenish-grey or olive-green. Unctuous to the touch. $\text{H.} = 3\cdot5$. Sp. gr. 2·623—2·652. A specimen from Chesterfield Hollow had the following composition:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	CaO.	Li ₂ O.
46·80	32·52	2·33	0·04	0·04	0·48	0·77	0·32
Na ₂ O.	K ₂ O.	H ₂ O.	Org. matter.				
0·78	7·24	7·66	1·14	=	100·12		

leading to the formula $\text{H}_6 \text{K}_2 \text{Al}_4 \text{Si}_5 \text{O}_{20}$, or $\text{H}_2 \text{K}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18} + 2\text{Aq.}$, which agrees with that of killinite from Killiney Bay in Ireland.

The following pseudomorphs after spodumene are also mentioned:—

- (1.) A pseudomorph consisting of vein-granite made up of muscovite, albite, and quartz, and traversed by large columns of cymatolite.
- (2.) Of greenish-yellow muscovite more or less intermixed with cymatolite.
- (3.) Of albite, generally intermixed with muscovite and quartz.
- (4.) Of quartz, rare, and containing more or less mica. H. W.

Arctolite: a Mineral from Spitzbergen. By C. W. BLOMSTRAND (*Jahrb. f. Min.*, 1881, 2, Ref. 32—33).—This mineral occurs in the form of bent plates of about 1 cm. thick in crystalline limestone. It is colourless or light green, and sometimes occurs in small prisms of 3—5 mm., having an angle of 124—126°. $\text{H.} = 5$; sp. gr. = 3·03; difficultly fusible. The mean of two analyses is:—

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.
44·93	0·38	23·55	1·24	13·28	10·30	1·73	0·79	3·54 = 99·74

giving the formula of prehnite $H_3R_2Al_2Si_3O_{12}$, or if the water is considered as basic, the general hornblende formula is obtained. Whether the angle measured is the prism angle of hornblende ($124^\circ 30'$) or the domal angle $\frac{3}{2}P\infty$ of prehnite ($127^\circ 17'$) remains to be determined.

H. B.

Mesolite and Scolecite. By O. LUEDECKE (*Jahrb. f. Min.*, 1881, 2, Mem. 1—40).—References are given to all previous papers on the subject, as also an historical account. Natrolite occurs in rhombic crystals, and according to Des Cloizeaux, scolecite is monosymmetrical, but mesolite occurs only in asymmetrical and twinned crystals. The author examined scolecite, and found it to contain as large a percentage of soda as of lime; thus it would appear to be mesolite, but it is monosymmetrical. To clear up this contradiction, typical mesolite crystals from Iceland were examined, but found to be single monosymmetrical crystals. Typical scolecite crystals from the Fellinen Alps were examined, and found to be asymmetrical twins, quite like Des Cloizeaux' mesolite; other crystals previously examined by Rose and Hankel, were found to be monosymmetrical twins, just as described by Rose. Hence there are both monosymmetrical and asymmetrical scolecites and mesolites, and they are isodimorphous. Since, from numerous analyses, mesolite appears as a mixture of scolecite and natrolite, it follows that the two latter must be isomorphous, and there must be mono- and a-symmetrical natrolities as well as rhombic scolecites and mesolites. In support of this view is the fact that natrolite crystals from Salesel and Aussig show depolarisation directions inclined $5-6^\circ$ to the prismatic edges; moreover, Des Cloizeaux says that the optical characters of galactile—which in composition resembles mesolite—agree with those of natrolite. Some of the details of the author's observations are as follows:—

Monosymmetrical scolecites.—Crystals were obtained which had been examined by Riess and Rose, and were obtained from Iceland, and also some crystals from Kandallah, which Hankel had used in his thermoelectrical determinations; none of the specimens contained sodium. The clinopinacoid is divided by a fine line, towards which striations run, making together an angle of $24-26^\circ$. Sections parallel to the clinopinacoid show the twin nature of the crystals, the twin plane being $\infty P\infty$. The depolarising directions of the two crystals make together in $\infty R\infty$ an angle of $21-23^\circ$ (i.e., those from Iceland), or $31-33^\circ$ (those from Kandallah); these directions do not lie symmetrically to the fine line on the surface of $\infty R\infty$, but vary in position, and this is presumably due to irregularities of growth, for the monosymmetrical nature of the crystals is proved by a section perpendicular to $\infty R\infty$ and to ∞P . The planes of the optic axes in the two crystals are inclined $32-33^\circ$ to each other, and are at right angles to $\infty R\infty$; the optical axial angle itself, measured in an Adam's polariscope, is $34^\circ 35'$ for Li, $35^\circ 36'$ for Na, and $36^\circ 36'$ for Tl; similar values were found by Des Cloizeaux; the dispersion is horizontal and $\rho < \nu$. The form of the crystals is $\infty P. \infty R\infty$. — P, often also P; the faces $-3R3$ and $-3P$ are very small when they occur. The crystals from Kandallah showed, in addition, the forms $-P\infty$ and

$\infty P\infty$; some of these faces allow of accurate measurement, and gave the following results:—

$\bar{a} : \bar{b} : \bar{c} = 0.9729 : 1 : 0.3390$; $\beta = 89^\circ 5'4''$. G. Rose, mean of many measurements.

Do. $= 0.9767 : 1 : 0.3409$; $\beta = 89^\circ 30'3''$. Author, mean of several measurements on crystals from Iceland.

Do. $= 0.9744 : 1 : 0.3406$; $\beta = 88^\circ 58'6''$. Author, a single crystal from Kandallah.

But the author remarks that as Rose measured many crystals, it would be better to retain his axial relations for monosymmetrical scolecites.

Asymmetrical Scolecites.—Crystals were examined from Shattigen Wichel, on the Fellinen Alps, behind Bristenstock. They are small prisms, 0.2—1.8 mm. in diameter, terminated by four pyramidal faces, and are well formed; some are transparent, others milky. That they are truly scolecite is shown by the analysis:—

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.
46.43	25.89	14.07	0.49	13.24

The crystals from Etzlithalle are free from sodium. Those from the Faroe Islands were small four-sided prisms without terminations; they were free from sodium, and could only be examined optically; they showed the same behaviour as the other specimens.

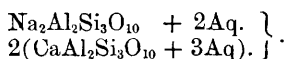
A section parallel to the obtuse edge of the prism is seen to consist of two parts, whose depolarising directions lay very approximately symmetrical to the obtuse edge of the prism, and make with it—towards the free end of the prism—angles of 16° . Sections parallel to the other prismatic edge (*i.e.*, parallel to $\infty R\infty$), show throughout the same depolarisation direction, which makes with the prismatic edge above an angle of $7-8^\circ$, hence the crystals must be asymmetrical. Sections perpendicular to the prism consist of two parts, whose combination edge is parallel to the brachypinacoid, and with which edge depolarising directions and the planes of the optical axes of the two halves make angles of about $8-9^\circ$. The double refraction is negative and $\rho < v$; the axial angles measured in the Adam's polariscope were $35^\circ 17'$ for Li, $36^\circ 20'$ for Na, and $38^\circ 22'$ for Tl. Crystallographically the twin plane and the plane of symmetry is $\infty P\infty$, and the forms are ∞P_1 , $\infty P_1'$, P on the right side, and the same forms, but in twin position, on the left. From the mean of many measurements on Shattigen Wichel crystals, and from measurements on a single crystal from Etzlithalle, the axial relations for the upper front right octant were calculated, viz.:—

$\bar{a} : \bar{b} : \bar{c} = 0.9712 : 1 : 0.3576$; $\alpha = 88^\circ 30'1''$; $\beta = 90^\circ 41'3''$;
 $\gamma = 89^\circ 49'2''$; and

$\bar{a} : \bar{b} : \bar{c} = 0.9676 : 1 : 0.3484$; $\alpha = 90^\circ 56'3''$; $\beta = 90^\circ 37'1''$;
 $\gamma = 89^\circ 52'8''$.

Mesolites.—The author had not an opportunity to examine asymmetrical crystals as described by Des Cloizeaux. Monosymmetrical

crystals were examined from (1) Iceland, the same consisting of diverging bundles of prismatic crystals having free ends, and the whole forming the lining of a large cavity in basalt, but between the two is a clayey substance, which could not be removed, and so influenced somewhat the composition, which agrees, however, with Rammelsberg's formula:—



(2). Delicate needles from Pfasterkaute. The analyses gave:—

	SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	H ₂ O.
(1.).....	46.58	27.57	9.11	0.08	3.64	12.94
Calculated..	46.32	26.40	9.61	—	5.32	12.35
(2.).....	43.83	29.04	7.84	—	7.80	11.75

Optical examination shows that the crystals were simple; examined through the prismatic faces, the depolarising direction makes an angle varying from 4—24°, but the inclination was the same in both those adjacent faces which enclose an angle of 91° 10' (crystals No. 2). Viewed through the clinopinacoid the depolarising direction makes an angle of 9° with the front prismatic edge below; a section parallel to $\infty P\infty$ proved the crystals to be monosymmetrical. The forms observed are ∞P . — P . P . and $\infty R\infty$, and the prismatic and pyramidal faces were striated by a prism $\infty R_{1\frac{1}{3}}^{\frac{1}{3}}$ or $\infty R_{1\frac{1}{4}}^{\frac{1}{4}}$, and a secondary pyramid respectively. The calculated axial relations are—

Crystals No. 1. $a : b : c = 0.9079 : 1 : 0.3226$; $\beta = 87^\circ 53.6'$.

„ No. 2. „ = $0.9241 : 1 : 0.3375$; $\beta = 85^\circ 57.8'$.

These values agree fairly with those of monosymmetrical scolecite; but if $\infty R_{1\frac{1}{3}}^{\frac{1}{3}}$ and the secondary pyramid be considered as the primary prism and pyramid, then the values for mesolite and scolecite agree much more nearly.

H. B.

Analysis of a Mineral resembling Thorite. By P. COLLIER (*Journal of the American Chem. Soc.*, 2, 73).—This mineral, probably from the iron district of Champlain, is similar in colour, streak, hardness, density, &c., to thorite or orangite. An analysis by H. B. Parsons gave:—

SiO ₂ .	ThO.	PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	U ₂ O ₃ .	CaO.
19.38	52.07	0.40	0.33	4.01	9.96	2.34
	MgO.	Na ₂ O.	H ₂ O.			
	0.04	0.11	11.31	= 99.95		

On account of the large proportion of uranic oxide in the mineral, the author proposes to name it *Uranothorite*.

H. W.

Rosterite, a New Variety of Beryl from Elba. By G. GRAT-TAROLA (*Jahrb. f. Min.*, 1881, 2, Ref. 167).—The ordinary beryls from Elba are for the most part hexagonal prisms with base and end-face; of various colour, mostly light; the prismatic faces are striated

sometimes finely in the longitudinal direction, not unfrequently also transversely, and they often exhibit plumose striation (*striatura a spina di pesce*). The base is shining, apparently smooth, but nevertheless characterised by irregular undulations. The crystals are implanted in the geode by one end, and in some geodes the majority of the crystals are longer than they are broad. In rosterite, on the other hand, the length rarely exceeds the breadth, most of the crystals indeed consisting of low hexagonal tablets. The faces do not exhibit either of the three above-mentioned varieties of fine striation, but a network of deep longitudinal and transverse striations, consequent on the building up of the large crystal by the union of a great number of smaller hypoparallel individuals. The same may be observed on the basal face, which is not so smooth as in beryl, but often appears somewhat convex, from the presence of a number of small faces, arranged with a certain degree of regularity in six sections, corresponding with the six prismatic edges, and forming with the second prism a system of parallel striæ. These cut one another in six edges, and unite the centre of the base with the middle points of the radial edges. Frequently, however, more complex patterns occur on the base, arising from the mutual penetration of parts of the individual sectors. Further distinctions between rosterite and true beryl are, that in the former the prismatic faces are never surmounted by distinct dihexahedral faces of the first order, and that the faces resting on the edges are always very small. Lastly, the crystals of rosterite are always implanted by their sides, never by one extremity, so that every crystal has both its ends developed. The colour is mostly light rose-red.

Common beryl, according to the author, is not uniaxial. A section cut parallel to the base exhibits, in parallel polarised light, a complex polychromatic image of the many variously orientated biaxial individuals, which show themselves as such also in convergent light by lemniscates and hyperbolas. In rosterite, on the other hand, the basal plate shows, in parallel polarised light, six differently coloured sections, placed similarly to the six prismatic faces, and therefore opposite to the crystallographic sections produced by the striation. These sections vary in brightness, as usual, on rotation, each opposite pair corresponding in phase. In convergent polarised light, lemniscates and hyperbolas are seen variously disposed in the different sections, some of the axial planes being parallel to the prism faces, whilst others are inclined to them at angles up to 7° . Axial angles about 15° . The great polyhedry of the prism-faces of rosterite does not admit of exact measurements, but approximate determinations gave $120-123\frac{1}{2}^{\circ}$ for the prismatic angles. The author regards the biaxial character of the mineral as established beyond doubt.

The chemical analysis of rosterite, which, however, cannot be regarded as quite satisfactory, gave the following results:—

	I.	II.	III.	IV.
Water	Undet.	3·07	2·32	2·03
Silica	61·97	60·26	62·88	61·34
Alumina	21·93	21·18	17·09 } *	23·20
Glucina	8·62	9·71	15·97 } *	8·81
Lime	0·42	2·55	2·99	2·19
Magnesia	1·26	1·57	2·62	0·50
Potash	} Undet. {	0·58	} Undet. {	1·00
Soda		Undet., but		
Lithium		distinct reaction		
	94·20	98·92	103·87	99·07
Sp. gr.	2·77	2·74	2·77	2·75

Analyses I and II relate to the peripheric portion of a rose-coloured mixed crystal (the only one known) consisting of a nucleus of beryl, enclosed in a coating of rosterite; III is the central portion of this crystal; IV, a small typical crystal of rosterite. Remarkable in all the analyses is the presence of water and alkalis and the small amount of silica, which in other analyses of beryl usually ranges from 66 to 69 per cent., and of alumina, which is generally given as $17\frac{1}{2}$ to 20 per cent. Another peculiarity of rosterite is the small quantity of glucina, which in other beryls varies from 12 to 14 per cent.

H. W.

Composition of some Coral Limestones, &c., from the South Sea Islands.—By A. LIVERSIDGE (*J. Roy. Soc., N.S.W.*, 14, 159—162).—1. *Reef Coral*, New Hebrides: A white crystalline limestone, like aragonite on its fractured surface; made up chiefly of prismatic crystals, the remainder being coarsely crystalline like marble. Exhibits no trace of organic structure, but is coated externally with purple organic matter, which burns when heated on platinum foil. Before the blowpipe the limestone whitens and falls to pieces like aragonite. Found on Vati or Sandwich Island, at the level of high-water mark. 2. *Red Reef Coral*, New Hebrides: Reddish-brown, intermixed with white portions, due mostly to fragments of coral and shell disseminated through the mass, and giving the rock very much the appearance of a bone breccia from a cave-deposit. 3. *Coral limestone*, Duke of York Island, one of the Union group: from a raised reef, 100 feet above the sea-level.

* These numbers are inexact: hence the large excess.

	1	2.		3.
		I.	II.	
CaO	54.62	48.75	—	52.094
MgO	0.08	3.36	2.33	0.861
K ₂ O	traces	0.15	—	0.983
Na ₂ O	—	0.40	—	0.848
NaCl	1.02	—	—	—
Al ₂ O ₃	0.23	2.81	{ 1.69 0.62	1.973
Fe ₂ O ₃	traces			trace
SiO ₂	0.51	1.17	—	0.789
„ soluble.....	0.21	0.17	—	—
P ₂ O ₅	trace	trace	trace	—
CO ₂	42.32	43.22	41.25	41.679
Cl	—	trace	0.12	trace
Organic matter.....	—	—	—	0.500
H ₂ O (hygroscopic)	0.26	0.50	—	0.019
Loss	0.75	—	—	0.254
	100.00	100.53	—	100.000

4. *Tuff-rock* (?), from the Island of Vati, New Hebrides, 525 feet above the sea-level. Greyish-white, readily friable. The analysis shows that it is not a limestone, though it may have been found to contain corals. Effervesces feebly with acids. The combined water was determined by ignition of the rock to complete fusion, allowance being made for the carbonic anhydride driven off at the same time.

5. *Tuff-rock* from the shore below high-water mark of Port Sandwich, Mallicollo, New Hebrides. Colour greyish. Fracture large conchoidal with dull smooth-looking surfaces. Very fine-grained. Soft, and easily scratched with a knife. Emits a dull sound when struck. Sp. gr. = 2.186. Mainly a silicate of alumina.

	4.		5.
	Sol. in acid.	Insol. in acid.	
SiO ₂	0.70	56.56	62.57
Al ₂ O ₃	6.60	14.80	28.82
Fe ₂ O ₃	0.56	—	trace
CaO.....	1.66	trace	0.74
MgO	trace	6.76	trace
K ₂ O and Na ₂ O	traces	—	1.45
H ₂ O, combined	7.58	—	1.71
„ hygro. (at 100°) ..	3.68	—	4.41
CO ₂	1.04	—	0.30
Loss	—	0.06	—
	21.82	78.18	100.00
	100		H. W.

Composition of Tuscan Serpentine. By A. COSSA (*Mem. dell. Accad. dei Lincei* [3], 5; *Jahrb. f. Min.*, 1881, 2, Ref. 237).—
I. The Serpentine of Calagrande, Monte Argentaro, Province of Grosseto,

containing enclosures of bastite, appears from its structure to have been formed of rhombic pyroxene. The bastite is associated with microscopic hornblende. The ore on the rock consists of titaniferous iron ore. Sp. gr. = 2.992 at 19°; in another experiment 3.020 at 17°.

II. *Serpentine from the Gabbro-field of Livorno*, originating from a bronzite-peridotite, partly with unaltered olivine. Enclosed minerals, bastite and microscopic magnetite. Sp. gr. = 2.57 at 16°.

III. *Serpentine from Rio Marina*, on the right bank of the Riale in Elba; almost pure olivine-serpentine, with microscopic bastite and magnetite. Sp. gr. = 2.59 at 16°.

IV. *Serpentine from Rio Alto, Elba*.—Originating from bronzite-peridotite, with enclosures of bastite; moderately decomposed, and traversed by thin, colourless, nearly round, undeterminable laminae. Sp. gr. = 2.6.

V. *Serpentine from the great mass on the road from Rio to Longone, Elba*.—Resembles the preceding, but is richer in bastite. Sp. gr. = 2.61.

VI. *Serpentine from the limestone bed at the Port of Portoferraio*.—Contains no trace of olivin, but, like the Argentaro rock, has been produced from bronzite. Sp. gr. 2.53—2.55 at 17°.

	I.	II.	III.	IV.	V.	VI.
Silica	33.863	40.892	39.21	39.58	39.38	39.932
Titanic oxide	0.686	trace	—	—	trace	trace
Phosphoric oxide ..	1.310	—	—	—	—	—
Alumina	7.562	1.156	trace	—	trace	trace
Ferric oxide	12.073	4.959	7.87	7.65	8.26	6.899
Ferrous oxide	15.345	4.770	2.63	4.13	3.67	3.750
Manganous oxide ..	trace	trace	trace	trace	trace	trace
Magnesia	18.692	35.937	36.92	36.37	35.62	36.824
Lime	4.514	trace	trace	trace	trace	—
Chromic oxide	—	0.232	0.27	trace	trace	0.183
Loss by ignition....	5.868	11.909	12.54	12.72	12.85	13.047
	99.913	99.855	99.44	100.45	99.78	100.635

H. W.

Metamorphoses of Nephelin Rocks. By C. v. ECKENBRECHER (*Jahrb. f. Min.*, 1881, 2, Ref., 231).—The author has made a chemical and microscopical examination of a specimen of phonolite from Zittau, relatively poor in nephelin, and having a very distinct crust produced by weathering, with the view of understanding the transformations which it has undergone. The fresh, dark green, thin, slaty phonolite (Anal. I), the sanidin crystals of which are not tabular according to ∞P , as generally assumed, but prismatic according to $0P$ and ∞P , is coated with a fine-grained, light grey, bluish shimmering efflorescence-zone, in which, on account of its light colour, the magnetite of the phonolite is seen more distinctly than the sanidin. Outside this zone is another (B) 1 cm. thick, of soft texture and yellowish colour, with scaly striations on the surface, and containing a small

quantity of sanidin; outermost of all is a very porous zone (C), 2 cm. thick, white with a few yellow spots, and of chalky aspect.

	I.	A.	B.	C.
Silica	56·638	63·561	61·314	58·408
Alumina	23·542	17·856	24·514	24·077
Ferric oxide ..	4·463	3·992	1·959	0·541
Lime	2·801	1·199	1·579	1·381
Magnesia	0·007	0·201	0·409	1·582
Potash	5·392	7·101	6·536	6·305
Soda	6·083	5·897	2·353	3·170
Water	0·484	1·227	2·019	3·745
	99·410	101·034	100·683	99·209
Sp. gr.	2·60 (15°)	2·63 (16°)	2·43 (17°)	2·42 (17°)

In I, chlorine and manganese were detected qualitatively, and the absence of sulphuric acid was demonstrated. In A no indications were found of either chlorine, sulphuric acid, or manganese. The water was in all cases estimated as loss by ignition. According to these results, the phonolite-constituent belonging to the hauyn-group is sodalite, and not hauyn or nosean—as found by Werveke in African phonolites;—in B this constituent is completely decomposed. Microscopical examination shows that the fresh phonolite is made up of a large quantity of sanidin, and small quantities of nephelin, sodalite (already partially zeolised), augite and manganite. In A the nephelin is zeolised, and even the sanidin is no more fresh in all parts, whilst the augite is quite bleached, and with the exception of a few double-refracting spots, is converted into an isotropic substance (? opal) intersected by yellow bodies.

In connection with his phonolite studies, the author has also examined chemically and microscopically the natrolite of Brevig and Frederiksvärn, both in isolated masses and in the rock. It is made up essentially of tufts or fork-shaped groups of fibres, between which is inserted a colourless substance with brilliant aggregate-polarisation (apparently a mixture of quartz and calcite). Both in the natrolite itself and in these colourless aggregates, there occur irregularly bounded strongly refracting sections of a mineral having a monotomic cleavage, and appearing, from comparative studies of the dillnite of Schemnitz, to be identical with the diaspor which was detected chemically in natrolite by Scheerer, Pisani, and Sämann (*Rammelsberg's Mineral Chemie*, 2te Auflage, 2, 631). An analysis of this yellow natrolite (sp. gr. 2·39) gave 46·812 per cent. SiO_2 , 27·335 Al_2O_3 , 15·689 Na_2O , and loss by ignition 10·198, together with traces of iron and lime.

Microscopic examination of the matrix of the natrolite, showed, as previously found by Blum, that the latter has been formed chiefly from elæolite, partly also from veins of albite in microcline, and from the latter mineral itself. This confirms the view first enunciated by Dauber, and adopted in certain cases by Blum and Herter, that natrolite has been formed from felspar.

H. W.

The Rock of Monte Tajumbina in Peru. By C. HÖPFNER (*Jahrb. f. Min.*, 1881, Mem. 164—192).—This mountain is of considerable extent and has several peaks, the western and eastern summits attaining a height of 4,124 meters. The western foot is surrounded by a marshy lagune-plain, from which rise a number of isolated lava rocks.

The rocks of the different parts of the mountain are very much alike in many respects; nevertheless certain differences are observable, due especially to various rapidities of solidification of the fluid lava, and to differences in the weathering of the solid rock. The specimens examined, 34 in number, all exhibited a porphyritic development, but they varied in depth of colour, and some were richer than others in large crystals of felspar. All the rocks exhibit a more or less porous, sometimes almost scoriaceous structure, the pores having the form, not of roundish cavities, but of irregular cracks, in which brown products of decomposition are frequently deposited.

The ground-mass of the rock in which the porphyritic constituents are imbedded, has a dark-grey colour in the fresh state, generally changing to red by weathering, or to a light-grey when the weathering is very far advanced. It is seen by the naked eye, and still better with a lens, to be composed of felspar, hornblende, augite, and magnetite in small and extremely minute crystals, the magnetite being closely aggregated in some parts, more sparingly in others. Among the imbedded crystals plagioclases of various sizes, but averaging 4 mm. long and 3 mm. broad, are especially abundant, and occupy altogether about as much space as the compact ground-mass. The course of decomposition of the felspars cannot always be traced, but in some parts it is seen to begin at the central portion.

Magnesia-mica occurs in much smaller quantity than the plagioclase, but regularly imbedded, and crystallised in dark-coloured six-sided plates, having a rusty tint due to incipient decomposition. Hornblende is also abundant, recognisable by its lustre, hardness, and cleavage; augite is difficult to recognise. Quartz is distinctly visible in all the specimens, excepting the denser ones from the lagunes, and even in these the presence of free silica may be recognised.

These characters show that the rocks in question belong to the group of quartz-andesites; moreover they are quartz-augite andesites, inasmuch as hornblende and mica are present in them for the most part only in comparatively large crystals, whereas the augite, which is always present, seldom forms large separate crystals, but is an essential constituent of the ground-mass.

The results of the microscopical and chemical examination of the rock are summarised by the author as follows: (1.) Microscopical examination renders it probable that Monte Tajumbina has been produced by a single great eruption.—(2.) At all points of this vast mass of rock, the order of crystalline separation has been the same, whence it follows that this order has been determined, not so much by pressure, &c., as by the chemical composition of the rock and by the temperature to which it was subjected.—(3.) All the specimens examined suggest the idea that the formation of felspar began with

anorthite.—(4.) The magnesia-mica appears to have been formed at a very early stage, whereas the separation of augite appears to have taken place after the beginning and before the end of the plagioclase formation. The separation of the singulosilicates (metasilicates) MgSiO_3 , &c., began with hornblende and finished with augite. The more acid feldspars and quartz were probably the last to solidify.

The chemical analysis of the compact rock from the lagunes gave:—

SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
63.19	18.65	4.01	1.88	0.13	1.20	4.86	3.69	1.95
		TiO_2	P_2O_5	Loss by ignition.				
		0.18	0.25	0.07 = 100.06				

From this the author calculates the number of molecules of the several constituents which make up 100 mols. of the rocks, and infers that it must contain 23.8 mols. per cent. of free silica. H. W.

Note on a Crystallised Slag Isomorphous with Olivine. By A. E. ARNOLD (*Jahrb. f. Min.*, 1881, 2, Ref. 30—31).—The crystals were found in the cavities of the slags produced by Hollway at Penistone, England, in July, 1878, when experimenting on the reduction of metallic sulphides. Their composition is almost exactly that of an iron olivine in which a part of the ferrous oxide is replaced by ferrous sulphide.

	SiO_2	FeS	FeO	Al_2O_3	Cu	MnO, ZnO	
(1.)	28.99	—	—	—	—	—	sp. gr. = 4.19
(2.)	29.06	6.10	61.34	0.60	0.14	2.78 = 100.02;	sp. gr. = 4.22
(3.)	29.08	6.09	64.82	—	—	— = 99.99	—

the last numbers being calculated from the formula $\left. \begin{matrix} 13\text{FeO} \\ \text{FeS} \end{matrix} \right\} 7\text{SiO}_2$.

The author then endeavours to show that the sulphur is an essential constituent, *i.e.*, the substance is a sulphosilicate. In relation to this, two analyses by J. E. Stead are quoted of similar slags obtained in the same experiment, and about 3 per cent. sulphur was found replacing oxygen. The crystal measured by C. O. Trechmann had the usual form $\infty\text{P} \cdot \infty\text{P}\infty \cdot 2\text{P}\infty$. H. B.

A Volcanic Breccia useful for a Top Dressing. By A. CARNOT (*Compt. rend.*, 93, 222—223).—The author has received from the department of Hérault specimens of an argilloalcalcareous deposit, which was separable into angular fragments of a greyish, and a paste of a yellowish-green, colour. Its composition was as follows:—

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	Loss on ignition.
43.30	15.60	18.00	11.00	0.40	0.80	traces	0.40	10.20

The mineral is attacked by acids with effervescence, and is slowly disintegrated by the action of air. It appears that this mineral is used for the doors of limekilns, but it has recently been suggested that

it would be suitable for a top dressing, more especially in the cultivation of the vine. This volcanic deposit is widely distributed, not only in the department of Hérault, but also in the large volcanic regions of Auvergne, Vivarais, &c. V. H. V.

A New Meteoric Iron from North Carolina. By W. E. HARRIS (*Am. J. Sc.* [3], 20, 324).—This mass, which was found on the 19th of July, 1879, at Lick Creek, Davidson Co., North Carolina, is of elongated round form and weighs 1·24 kilo., and is composed, according to analyses by J. L. Smith and J. B. Macintosh, of 93 per cent. Fe, 5·74 Ni, 0·52 Co, 0·36 P, and traces of sulphur, chlorine, and copper. It is covered with a scaly black-brown crust, and exhibits on its surface an oxidation of ferric chloride in yellow drops. Etching with acids does not produce any Widmanstätt figures, but brings to light a crystalline texture, shown by the development of faintly reflecting surfaces arranged in parallel order. H. W.

On a Meteorite which fell on the 26th of November, 1874, at Kerilis, Commune of Maël-Pestivien, Canton de Callac. (Côtes-du-Nord). By A. DAUBRÉE (*Jahrb. f. Min.*, 1881, 2, Ref. 182).—This stone, weighing 4·2 kilos., is of nearly parallelepipedal shape, and is covered with a thick black crust having a rough scarred surface, in which metallic granules are visible. On one part of the surface, cavities are observed, due to the action of strongly compressed gases. The fractured surface has a dark-grey colour with ochre-yellow specks. The meteorite has a sandy appearance, resulting from the agglomeration of particles of very various characters, some being rather large and of chalky whiteness, while others, more numerous, are of an ash-grey colour. Here and there spherules are observed as in chondrites, and round bronze-coloured grains. The entire mass is traversed by nickel-iron. The specific gravity of the meteorite is 3·51 at 15°.

Hydrochloric acid dissolves about 60 per cent. of this meteorite, the dissolved portion consisting of olivine, nickel-iron, and magnetic pyrites. The insoluble residue contains enstatite and chrome-iron ore. The examination of a thin section shows that the enstatite occurs in needles radiating from several centres and thus forms the globules. These moreover are enclosed in granular olivine, containing also nickel-iron and magnetic pyrites.

Daubrée regards this meteorite as most nearly related in its entire constitution to the meteorites of Limerick (September 10th, 1813), and Ohaba in Transylvania (October 10th, 1857), both of which belong to the class of grey chondrites. H. W.

Lithological and Geological Examination of the Meteorite which fell on the 15th of October, 1872, in the Neighbourhood of Soko-Banja in Servia. By S. MEUNIER (*Compt. rend.*, 92, 331).—This meteorite has an extraordinarily heterogeneous aspect, and may be compared in its structure with the Rhenish breccias. The author has examined the principal mass of the meteorite separately from the spherules, and regards the former as analogous to the

meteorites of Pegu and Scarsmont, the latter with those of Erxleben, Ensisheim, &c., and comes to the conclusion, that notwithstanding the great mineralogical resemblance of the spherules and the ground-mass, the former must be regarded as portions of a primitive rock, whereas the latter has been formed by the disintegration of primary rocks, and recombination of the fragments. Cracks and clefts occurring on the spherules indicate that they were subjected to the actions of mechanical forces, such as pressure, &c., prior to the formation of the ground-mass. In these clefts and on the small interstices of the ground-mass, nickel-iron has been deposited, its formation being due to the action of vapours of corresponding metallic compounds which have penetrated the structure. The author regards the formation of this meteorite as an additional indication of the analogy between cosmical and terrestrial geology.

H. W.

Synthetic Imitation of Meteoric Nickel-iron. By S. MEUNIER (*Jahrb. f. Min.*, 1881, 2, Ref. 184).—One of the best established facts regarding meteorites is, in the author's opinion, that they have not been formed by fusion. If in inquiring into the formation of meteorites, we take into account the secondary, as well as the principal constituents of those bodies—as Daubrée has done in his explanation of the formation of tin-ore deposits—we find ourselves compelled to assign to ferrous chloride, which appears only as a subordinate constituent, and to hydrogen retained by the iron, a certain part in the formation of meteorites. And in fact, the author, by means of these bodies acting at comparatively low temperatures, has succeeded in producing iron, which in its properties exactly resembles meteoric iron, and further by appropriate modification in the addition of nickel chloride, in producing kamacite and tænite. Lastly, by depositing one of the modifications of nickel-iron just mentioned upon the other, he has obtained a product exactly resembling meteoric iron and exhibiting distinct Widmanstatt figures.

The author has also obtained formations analogous to the meteoric iron of spongy aspect having portions of silicates enclosed in its mass, and therefore having the structures of Pallasites; and, lastly, he has produced artificially the structure of ordinary meteorites containing enclosed iron which has retained hydrogen in its mass. The low temperature employed in all these preparations points to a similar mode of formation of natural meteorites.

H. W.

Law of the Formation of Saline Mineral Waters. By DIEULAFAIT (*Compt. rend.*, 92, 756).—By a long study of the saline springs of Western Europe the author has been led to the following general law of their formation.

The saline mineral waters of Western Europe are mineralised in the salt-bearing strata of the trias and tertiary formation. The substances which mineralise these waters were formerly contained in ordinary seas and have been deposited by simple evaporation. According as the evaporation of these ancient seas was more or less advanced, so the springs passing through the deposits will vary in composition from water containing gypsum to water containing all the substances

present in sea-water. The remainder of the paper is purely geological. C. W. W.

Felspar from the Rhombic Porphyry of Christiania. By O. MÜGGE (*Jahrb. f. Min.*, 1881, 2, Mem. 107—120).

On the Artificial Formation of the Diamond. By J. B. HANNAY (*Proc. Roy. Soc.*, 30, 188 and 450—461).

Existence of Boric Acid in Saline Lakes and Natural Saline Waters. By DIEULAFAIT (*Compt. rend.*, 93, 224—226).—The author's theory on the formation of boric acid renders probable the presence of that acid in saline lakes and mineral saline waters. The author has examined waters from various sources, and has found boric acid invariably present. The geological conditions were, however, widely different, but are separable into four distinct types. 1st. Igneous rocks, as in Tuscany. 2nd. Serpentine rocks, with gaseous emanations, as in the Engadine. 3rd. Serpentine rocks, without gaseous emanation, as in the Pyrenees. 4th. Calcareous and stratified districts, as in the south-east of France, the Alps. The author has further examined the celebrated mineral waters of Friedrichshall and Hombourg, both places being in a calcareous district traversed by volcanic rocks; and in both of them the presence of boric acid was indicated. V. H. V.

Hot Spring at Nabmoo, near Maulmain, British Bu. mah. By R. ROMANIS (*Chem. News*, 43, 191).—The spring was found in a thicket of bushes in the middle of rice fields, about two miles from the hills and one from the river bank. The soil is alluvial, with ridges of laterite and carboniferous limestone. The analysis gave the following results calculated as grams per litre of water:—

NaCl.	KCl.	CaCl ₂ .	MgCl ₂ .	SO ₃ .	Fe ₂ O ₃ .	CaCO ₃ .
10·446	0·344	2·218	0·855	0·109	0·002	0·175

Residue on evaporation 14·07 grams, and chlorine 8 grams per liter. D. B.

Water of Hot Springs in New Britain and the Fiji Islands. By A. LIVERSIDGE (*J. Roy. Soc., N.S.W.*, 14, 145—146).—The water from one of the islands of the New Britain group was of a yellow tinge, and smelt of hydrogen sulphide. It was neutral to test-papers when fresh, but afterwards became very faintly acid, probably from oxidation of the hydrogen sulphide. On evaporation to dryness at 100°, it left a residue amounting to 36,312 parts per million, or 2541·84 grains per gallon, which is about the same as that of average sea-water.

The water from the boiling springs at Savu Savu in Kandava, one of the Fiji Islands, was clear and colourless after deposition of a small quantity of suspended matter; it was scentless, but had a strong saline taste, and was neutral or very faintly alkaline to test-papers. Sp. gr. 1·0064 at 60° F. On evaporation to dryness, this water left a very white extremely deliquescent residue, which fused but did not

blacken on ignition, and therefore did not contain any appreciable amount of organic matter. The total solid matter in solution, after drying at 110° C., amounted to 8,320 parts per million, or 582.4 grains per gallon; but after the combined water had been driven off at a dull red heat, the residue was reduced to 7,813 parts per million, or 546.91 grains per gallon, *i.e.*, it lost 6.09 per cent.

The following table exhibits the composition of these thermal waters:—

	New Britain.			Fiji.		
	In 100 parts of residue.	Parts per million of water.	Grains per gallon.	In 100 parts of residue.	Parts per million of water.	Grains per gallon.
SiO ₂ , insoluble } SiO ₂ , soluble .. }	0.20	72.6	5.08 {	1.681	133.3	9.20
Al ₂ O ₃ and Fe ₂ O ₃ .	0.44	159.7	11.18	0.534	5.8	0.40
Al ₂ Cl ₆	—	—	—	0.534	41.7	2.92
CaSO ₄	1.39	506.2	35.43	1.646	128.6	9.00
CaCl ₂	2.24	813.4	56.93	4.770	372.7	26.09
MgCl ₂	4.71	1710.3	119.72	46.754	3652.9	255.70
NaCl	87.32	31707.6	2219.53	0.154	12.0	0.84
KCl	traces	—	—	42.171	3294.8	230.64
Combined water .	3.696	1342.2	93.97	1.756	137.2	9.60
Loss	—	—	—	—	—	—
	100.00	36312.0	2541.84	0.460	34.0	2.52
				100.000	7813.0	546.91

These analyses show that the salts dissolved in these waters consist mainly of chlorides, sodium chloride largely predominating in both, and the proportion of calcium chloride in the Fiji water being considerably in excess of the sulphate.

The Fiji water contains traces of carbonic and phosphoric acids, and only traces of ferric oxide mixed with the alumina. H. W.

Organic Chemistry.

Optical Rotatory Power of Organic Compounds. By T. THOMSEN (*Ber.*, **14**, 1654—1648).—A reply to Landolt's remarks (*Ber.*, **14**, 296 and 1048) on "Thomsen's Law of Multiple Proportions."

Optical Rotatory Power. By H. LANDOLT (*Ber.*, **14**, 1658).—A reply to T. Thomsen's answer to the author's former criticisms.

Caucasian Petroleum. By F. BEILSTEIN and A. KURBATOW (*Ber.*, **14**, 1620—1622).—The lower boiling portion of the petroleum

from the springs of Zarskije Kolodzy in Tiflis consists of butane, pentane, hexane, heptane, and small quantities of benzene and toluene. It differs entirely from the petroleum of Baku, which is composed of aromatic hydrocarbons. In the purification of the crude petroleum from Zarskije Kolodzy, by treatment with strong nitric acid, dinitrobutane was obtained as a bye-product. This compound crystallises in glistening needles (m. p. 96°) freely soluble in boiling alcohol, ether, carbon bisulphide, and light petroleum. W. C. W.

Deciline. By E. J. MAUMENÉ (*Compt. rend.*, **93**, 77—78).—When heated on a sand-bath with an equal weight of sulphuric acid, terebenthene forms a thick bulky black mass, almost entirely soluble in alcohol, and a small quantity of decilene distils over. With mercuric chloride a compound, $(C_{10}H_{16})_2HgCl_2$, is formed. These results are in accordance with the author's theory. When the mercury compound is distilled, its vapour exerts a highly dangerous poisonous action. C. H. B.

Active Propyl Glycol. By J. A. LE BEL (*Compt. rend.*, **92**, 532).—The propyl glycol, $CH_3.CH(OH).CH_2.OH$, was prepared from glycerate of soda, and rectified several times to free it from empyreumatic oils. A 3 per cent. solution was seeded, and allowed to ferment for several months.

Bacterium termo and two species of bacillus resembling the butyric ferment were produced in large quantities.

The liquid was rectified and the rotatory power was found to vary from $-4^{\circ} 35'$ to $-1^{\circ} 15'$ for 0.22 m.

Propionic and lactic acids were obtained as bye-products.

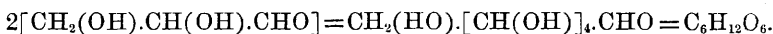
From this active propyl glycol, the author prepared propylene oxide, $CH_3-CH-CH_2$, which boiled at 35° , and had a rotatory power



of $+1^{\circ} 10'$ for 0.22 m.

C. W. W.

Oxidation of Glycerol by Nitric Acid. By PRZYBYTEK (*Bull. Soc. Chim.* [2], **36**, 145).—The author is of opinion that the oxidation of glycerol by nitric acid will give rise to a compound belonging to the glucose series, on the supposition that 2 mols. of glyceraldehyde (intermediate between glycerol and glyceric acid), unite to form a body of the same composition as glucose in the same way that acetaldehyde yields aldol:—



Although no glucose has been obtained from the reaction, yet two acids, apparently due to the oxidation of glucose, and resembling mannitic and saccharic acids, have been isolated. The presence of racemic and tartronic acids has been proved, but the principal product is glyceric acid. L. T. O S.

Sugar from the Tannin of the Oak Bark. By C. BÖTTINGER (*Ber.*, **14**, 1598—1599).—The author finds that the sugar obtained by

the action of dilute sulphuric acid on tannin from oak bark (*Annalen*, **202**, 269) is ordinary grape-sugar. It was separated from the quercite with which it was mixed, by treatment with hot alcohol.

W. C. W.

Inosite. By TANRET and VILLIERS (*Ann. Chim. Phys.* [5], **23**, 389—397).—The authors have investigated at length the properties of inosite extracted from the leaves of the walnut tree. It is prepared in the following manner:—The coarsely powdered leaves are treated with twice their weight of clear milk of lime, and then after standing for several hours, the mixture is diluted with cold water and treated with an excess of crystallised lead acetate. After filtering, ammonia is added as long as a precipitate forms. The precipitate is collected and treated with a slight excess of dilute sulphuric acid, and after removing the lead sulphate, the remaining acid is neutralised with baryta-water, and the filtrate after evaporation to a syrup, is poured into from ten to fifteen times its weight of alcohol (95 per cent.). The viscous precipitate which is thrown down, is obtained perfectly white after several crystallisations from water.

The maximum yield appears to be obtained from leaves gathered towards the end of August; 1 kilo. of dried leaves yielding 3 grams of the sugar. It forms clinorhombic prisms of the composition $C_{12}H_{12}O_6 + 2H_2O$, which effloresce in the air. The authors show by means of a table that the crystals of inosite obtained from various sources are crystallographically identical. The sp. gr. of the hydrated crystals is 1.524 at 15° C.; 1 part of inosite dissolves in 10 parts of water.

Action on Fehling's Solution.—If inosite is boiled for a few moments with Fehling's solution, the liquid remains clear, but becomes green; on allowing it to cool in the air, however, it gradually reassumes its ordinary colour. On prolonged boiling, a green precipitate is formed, the liquid being quite decolorised; on cooling, the precipitate redissolves. If the liquid is boiled for a long time, red cuprous oxide is formed. This action takes place more rapidly if a fresh quantity of Fehling's solution is added, for the green precipitate is formed only in the presence of small quantities of the alkaline copper solution. The fact that inosite reduces Fehling's solution must be taken into consideration in the examination of diabetic urine containing glucose.

Action of Nitric Acid.—By dissolving inosite in nitric acid and precipitating with sulphuric acid, crystallisable nitro-inosite is obtained; but if the solution is warmed, there is a copious disengagement of nitrous fumes. On evaporating, a white hygroscopic mass is obtained, which has the same weight as the anhydrous inosite employed. After washing with alcohol and drying at 100°, it evolves gas when treated with water. The gas is a mixture of nitrogen tetroxide, nitrogen, and carbonic anhydride. A solution of the compound becomes brown on heating, and loses its colour on cooling. In presence of a strong acid this change does not take place. Ammonia imparts to it a yellow colour, which is only gradually destroyed by organic acids. Mineral acids cause its immediate disappearance, which shows that the acid contained in the substance is tolerably strong, since it is not displaced by citric, tartaric, or acetic acid. It gives a rose coloration, with

calcium, barium, zinc, and mercury salts. Scherer's test for inosite is based upon this fact. The following is the best way of applying the test. The substance to be tested is evaporated almost to dryness with nitric acid in a platinum crucible, a drop of dilute calcium chloride is added, and the mixture again evaporated. If inosite be present, a rose coloration will be observed, especially on adding ammonia.

The barium salt of the acid is obtained as a reddish-purple precipitate on adding baryta-water to an aqueous solution. In an acid solution it has a greenish fluorescence, but appears reddish-brown when formed in presence of an alkali.

The authors find that inosite does not exist either in the very young or the old leaves. There is 1 gram of inosite per kilo. of dried leaves in June, and 3 grams per kilo. in August. Whenever it is found, it appears to be accompanied by a reducing sugar—in animal matter it is associated with glucose; in green haricot beans and in walnut leaves, it is found in company with a fermentable and reducing saccharine body.

J. I. W.

Optical Rotatory Power of Cane-Sugar in Alkaline Solutions.

By T. THOMSEN (*Ber.*, **14**, 1647—1650).—The rotatory power of a solution containing equal molecules of sodium hydroxide and cane-sugar diminishes with the strength of the solution, *e.g.*, $[\alpha]_D$ is 63.49 for a solution containing 2.112 per cent. of sugar, 60.55° for 15.72 per cent., and 58.64 for 42.71 per cent.

If the affinity of sodium hydroxide for water is eliminated, $[\alpha]_D$ is equal to 56.84.

The rotatory power of a dilute solution of sugar is decreased by the addition of sodium hydroxide. It attains its minimum of 56.84 on the addition of 8 molecules of alkali.

The molecular rotation of cane-sugar in its sodium compound is 194.26, *i.e.*, $12 \times 19.0 - 4 \times 8.4$.

W. C. W.

Rotation Constants of Cane-Sugar. By T. THOMSEN (*Ber.*, **14**, 1651—1653).—The author is of opinion that the value found by Schmitz in the case of cane-sugar for $[A]_D$, *viz.*, 64.156, is more accurate than 63.9035 as given by Toilems, since the former agrees more closely with the value calculated by means of the formula $n \cdot 19.0 + n' \cdot 8.4$.

Three different constants are now known: $[\alpha]_D$ for infinite dilution = 66.66; the true specific rotatory power (*i.e.*, calculated on the assumption that no solvent is present) $[\alpha]_D = 64.06$; and the rotatory power of cane-sugar in the sodium compound, $C_{12}H_{21}NaO_{11}$ $[\alpha]_D = 56.80$.

The observed and the calculated values for the molecular refraction agree closely.

	Formula.	Calculated. (<i>m</i>) _D .	Found. (<i>m</i>) _D .
Infinite solution.....	12×19.0	228.0	228.0
"True rotatory power" .	$12 \times 19.0 - 8.4$	219.6	219.1
Sodium compound	$12 \times 19.0 - 4 \times 8.4$	194.4	194.26

W. C. W.

Effects of Diastase on Starch-paste. By A. HERZFELD (*Bied. Centr.*, 10, 203—204).—According to the latest researches, the end products of this reaction are maltose and achroodextrin. In order to obtain crystallised maltose, the author recommends that a solution of the substance in hot 80 to 85 per cent. alcohol be left for some time in the cold, and the alcohol evaporated. Maltose probably forms an uncrystallisable hydrate in warm solutions, which is transformed into a crystalline anhydride in the cold. It is known that the saccharification of starch by diastase is most successful at a temperature of 65°, and is retarded by a higher temperature, and in this case, as shown by Maercker, no crystallisable maltose is obtainable; the author, however, has succeeded in separating a body which he believes prevents the crystallisation; his method is as follows:—The mass resulting from the saccharification is dissolved in a small quantity of water, and precipitated with 90 per cent. alcohol, the operation repeated 10 to 12 times, the residue dried on glass plates, scraped off, powdered, and dried at the same temperature; the alcoholic filtrate is distilled off, and its residue is treated in the same manner. This substance approaches very nearly to maltose in its reducing power. The substance which is precipitated by the alcohol is an uncrystallisable gum, only slightly more soluble in warm than in cold alcohol, and quite insoluble in strong alcohol and ether, but readily soluble in water; this property distinguishes it from maltose as well as from erythro- and achroo-dextrin. The author calls it malto-dextrin, and believes it to be identical with the γ -dextrin of Bondonneau. J. F.

Viscose. By A. BÉCHAMP (*Compt. rend.* 93, 78—81).—Viscose, the gummy substance formed by the viscous fermentation of cane-sugar, forms when dry a white friable substance of the same composition as starch, soluble in water in the cold, forming a gummy solution, from which it is precipitated by alcohol. The solution does not reduce Fehling's solution, and gives no blue coloration with iodine. Its rotatory power varies with the temperature, being +223·7 at 21°, 222·7 at 24°, and 219·8 at 38°. These values are somewhat near that for soluble potato-starch, 212°. Soluble cellulose is inactive, whilst the rotatory power of dextrans is much lower than that of potato-starch. Viscose yields two derivatives with nitric acid. When boiled with dilute sulphuric acid it is converted into a glucose and dextrans which are not fermented by yeast, but the reaction is somewhat slower than in the case of potato-starch. The dextrans produced vary in their degree of solubility in alcohol, and in their rotatory power, the extremes being +181·7 and 128·7. The glucose crystallises completely, and appears to be identical with that from potato-starch. Viscose is not acted upon by zythozymases, saliva, or sialozymases. During viscous fermentation, alcohol and acetic acid, and in some cases lactic acid, are formed in small quantity. Inverted sugar, glucose from potato-starch, and lævorotatory sugar, do not undergo viscous fermentation, but under the same conditions yield mannitol.

C. H. B.

Action of Triethylamine on the Monhaloid Paraffin-derivatives from Secondary and Tertiary Alcohols. By E. REBOUL.

(*Compt. rend.* **93**, 69—72).—Isopropyl iodide (b. p. 91—92°) is very slowly attacked by triethylamine in the cold, but when the two compounds are heated together in a closed tube at 100°, they react with formation of triethylammonium iodide and propylene. When 1 vol. isopropyl iodide, 2 vols. triethylamine and 4 vols. absolute alcohol are heated together, there is formed, in addition to propylene and triethylammonium iodide, ethyl-isopropyl ether, in amount varying with the temperature, a greater quantity being produced at 150° than at 100°. Tertiary bromobutane, a heavy colourless liquid, boiling without decomposition at 73—74°, obtained by the action of phosphorus tribromide on trimethylcarbinol, gives, when heated with triethylamine, triethylammonium bromide and butylene: in presence of alcohol, ethyl-pseudobutyl ether is also produced. It is evident that whilst the haloïd derivatives from the primary alcohols simply combine as a whole with triethylamine, the corresponding derivatives of secondary and tertiary alcohols, or at least their first terms, under the same conditions, lose their bromine or iodine as hydrobromic or hydriodic acid with simultaneous formation of an olefine. In presence of alcohol, this elimination takes place partly at the expense of the haloïd derivative only, partly at the joint expense of the haloïd derivative and the alcohol, the residues of the latter reaction uniting to form a mixed ether.

C. H. B.

Separation of Compound Ammonias. By E. DUVILLIER and A. BUISINE (*Ann. Chim. Phys.* [5], **23**, 289—356).—In the process devised by the authors, the compound ammonias are separated by means of the different solubilities of various well-crystallised salts, which readily admit of subsequent purification. It possesses decided advantages over the older method, in which the mixed ethers with very high and very similar boiling points had to be separated by fractional distillation. It consists essentially in subjecting the mixture of ammonias to two successive treatments with ethyl oxalate. The first is performed in an aqueous solution, when the monamines are precipitated in the form of oxamides. The bases remaining in solution are decomposed by boiling with potassium hydroxide, and the dried gas is dissolved in absolute alcohol. This solution is then again treated with ethyl oxalate, the diamines and any remaining trace of monamines being precipitated as ethyl oxamates. The triamines are obtained by subjecting the mother-liquor to distillation. As an example of the application of the process, the authors give an account of a research on the constituents of commercial trimethylamine.

Commercial Trimethylamine.—The precipitate which separates out from the aqueous solution consisting of oxamides of primary bases, can be divided into three portions by treatment with water. I. This portion is almost insoluble in water; when warm it floats on the surface, and on cooling forms a solid waxy mass. It consists of dibutyloxamide. The commercial trimethylamine therefore contains monobutylamine. The platinochloride resembles that of isobutylamine, as described by Wurtz. The authors therefore state that the base may be the isomeride of butylamine, although products obtained by the action of heat on organic substances generally belong to the

normal series. Portion II, which is fairly soluble in water, and separates out after the removal of the preceding body, consists of dipropyl-oxamide. When the quantity of this and the preceding substance is small, the authors make use of the comparative insolubility of the sulphates of the bases in alcohol for the purpose of separating them from the other amines. Portion III, which is deposited in white opaque needles or grains, consists of dimethyloxamide. By converting it into sulphate, and treating with boiling absolute alcohol, it is obtained quite pure, and yields pure methylamine by decomposition with potassium hydroxide.

The portion not precipitated by ethyl oxalate consists of diamines and triamines. It is decomposed by potassium hydroxide, and the dried gases passed into absolute alcohol. This solution is then titrated, and ethyl oxalate is added in sufficient quantity to precipitate the diamines, assuming the total alkalinity to be due to those bases. The alcoholic solution of the bases is poured gradually into ethyl oxalate, the flask being placed in ice, and continually shaken. The mixture is then distilled. *The distillate* contains the triamines. The only tertiary base found in commercial trimethylamine was trimethylamine itself. Its platinochloride forms large orange-red crystals. *The syrupy residue* after distillation consists of ethyl oxamates of diamines, together with a trace of monamines. They are separated by means of the different solubilities of their calcium salts. In this manner the authors separated from this portion propylamine and ethylamine. The mother-liquor from the calcium salts is treated with its own volume of ordinary alcohol. The precipitate thus formed can be separated into two portions by means of warm water. The less soluble portion consists of calcium monomethyloxamate; the more soluble is the dimethyloxamate. This indicates the presence of dimethylamine in commercial trimethylamine. The platinochloride forms small orange-red crystals. This base is the chief constituent of commercial trimethylamine; methylamine, propylamine, and butylamine come next in about equal proportions, then follows trimethylamine (5—10 per cent.), and finally ethylamine (2 per cent.).

Production of Methylamines.—The most convenient method of preparing methylamine is by heating methyl nitrate (1 mol.) with a solution of ammonia in methyl alcohol (1 mol.) in a closed vessel for 5 hours at 100°. Traces of dimethylamine, trimethylamine, and tetramethylammonium nitrate are formed in the reaction: when it is complete, the products are neutralised with sulphuric acid, and evaporated on a water-bath. The residue is distilled with potassium hydroxide, the gases being collected in hydrochloric acid. After evaporating and drying at 100°, the residue is treated with absolute alcohol to remove ammonium chloride, which remains undissolved. The soluble chlorides are decomposed by potassium hydroxide and reconverted into sulphates, which are then treated with absolute alcohol. This dissolves the sulphates of dimethylamine and trimethylamine with a trace of methylamine, and leaves a residue consisting of methylamine sulphate, together with a small quantity of ammonium sulphate. The methylamine is freed from impurities by treatment with oxalic ether. Dimethylamine and methylamine are separated

by the difference in the solubilities of calcium dimethyloxamate and monomethyloxamate.

Action of Methyl Nitrate on Methylamine.—When methylamine is heated at 100° in closed vessels with methyl nitrate the principal product of the reaction is tetramethylammonium nitrate. It is a non-deliquescent salt, extremely soluble in water, but less soluble in alcohol. It crystallises from an alcoholic solution in large scales. By acting on ammonia with methyl nitrate the same base is formed, but in smaller quantity, the chief product being methylamine.

Action of Methyl Bromide on Methylamine.—By acting on methylamine with methyl bromide (equal mols.) at 100° in closed vessels, tetramethylammonium bromide is obtained. Di- and tri-methylamine are formed in small quantities.

Action of Methyl Iodide on Methylamine.—The action is similar to that of the bromide. Tetramethylammonium iodide and traces of di- and tri-methylamine are formed.

Action of Methyl Bromide on Ammonia.—The reaction resembles that of the corresponding nitrate on ammonia. The principal product is methylamine, the other three bases being formed in small quantities.

Preparation of Dimethylamine.—The authors consider that the best source of dimethylamine is commercial trimethylamine. The various processes proposed by Baeyer, Caro, and Mertens, are not profitable.

Preparation of Trimethylamine.—Trimethylamine is best obtained by decomposing tetramethylammonium iodide with silver oxide, and submitting the hydroxide so obtained to dry distillation. It is readily obtained quite pure in the following manner:—A concentrated solution of tetramethylammonium nitrate is heated with an excess of a saturated solution of barium chloride, barium nitrate is precipitated, and separates almost completely on cooling: the last traces, however, are removed by adding alcohol to the solution. It is then evaporated to a syrup, and mixed with boiling alcohol: on cooling, the unattacked tetramethylammonium nitrate separates out, leaving the chloride in solution. The latter is then decomposed with silver oxide, and the hydrate distilled.

Tetramethylammonium nitrate heated with soda-lime yields ammonia, methylamine, dimethylamine, and trimethylamine. A *résumé* of the processes for preparing the methylamines shows that—1. Methylamine is obtained by the action of ammonia on methyl nitrate. 2. Dimethylamine is obtained from commercial trimethylamine. 3. Trimethylamine is prepared by decomposing salts of tetramethylammonium.

Production and Separation of Ethylamines.—In preparing diethyloxamide according to Wallach's method, the authors noticed that diethylamine in presence of ethyl oxalate yields ethyl diethyloxamate, which latter, being unstable in presence of water, is partially saponified, and yields diethyloxamic acid, which in its turn is decomposed with formation of acid oxalate of diethylamine.* The authors have made use of this fact in separating ethylamines. Methylamine yields a

* This is the well known method of Hofmann, published in 1864 (*Proc. Roy. Soc.*, 11, 66; *Phil. Mag.* [4], 22, 477).—ED.

similar body; but as it does not crystallise well, it is not advantageous to attempt the separation by means of it. Ethylamines are obtained by acting on an alcoholic solution of ammonia with ethyl chloride at 100° in closed vessels. The principal products are di- and tri-ethylamine. The ammonium chloride is first removed, and the ethylamine is then separated by means of ethyl oxalate. On decomposing the precipitate with potassium hydroxide the base is obtained pure. The mother-liquor from the diethylxamide is boiled for some time; on cooling, acid oxalate of diethylamine separates out, and this, on decomposition with potassium hydroxide, yields diethylamine. The filtrate from the acid oxalate still contains small quantities of the salt. It is therefore decomposed with alkali and the bases which distil over are dried, dissolved in alcohol, and treated with ethyl oxalate. After standing for a day, the alcohol and trimethylamine are distilled off. The residue is treated with milk of lime, and after filtering off the calcium mono- and di-ethylxamate, the liquid is treated with alcohol, which precipitates the remainder of the calcium salts: these salts are treated with boiling water, when the calcium salt of monoethylxamic acid is dissolved, and separates out on cooling in large crystals. The filtrate from the mixed calcium salts is concentrated, and on cooling calcium diethylxamate crystallises out; this is washed with ether to free it from traces of diethylxamide, and recrystallised from alcohol, from which it separates in fine radiating needles. They are very soluble in water and alcohol, but insoluble in ether. On decomposition with potassium hydroxide, they yield pure diethylamine.

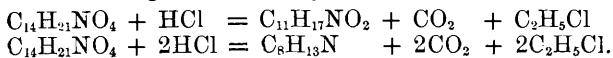
The authors find that tetrethylammonium chloride is formed by the action of ethyl chloride on alcoholic ammonia. Thus this same reaction yields the four bases,—mono- and di-ethylamine in large and equal quantities, together with smaller amounts of triethylamine and tetrethylammonium chloride.

In the hope of obtaining principally triethylamine, the authors acted on ammonia with ethyl iodide in closed vessels, and then when the action was complete, after separating the ammonium chloride, they again treated the ethylamines with ethyl chloride. After separating the mono- and di-ethylamine the hydrochloride of triethylamine crystallises in fine needles. It yields a platinochloride, which forms large orange rhombohedral crystals, $(\text{NEt}_3\text{HCl})_2, \text{PtCl}_4$. In the above reaction a considerable quantity of tetrethylammonium chloride is formed; it can conveniently be employed for the preparation of triethylamine by decomposing with silver oxide. The relative amounts of the bases formed in the reaction are about 4 of triethylamine, 2 of mono- and di-ethylamine, and 1 of tetrethylammonium chloride.

J. I. W.

Condensation Products from Aldehydammonia and Ketone Derivatives. By H. HANTZSCH (*Ber.*, **14**, 1637—1638).—By the action of zinc chloride on a mixture of ethyl acetoacetate and aldehydammonia, a compound of the composition $\text{C}_{14}\text{H}_{21}\text{O}_4\text{N}$, is produced, $2\text{C}_6\text{H}_{10}\text{O}_3 + \text{C}_2\text{H}_7\text{ON} = 3\text{H}_2\text{O} + \text{C}_{14}\text{H}_{21}\text{O}_4\text{N}$. This substance melts at 131° and boils at 310° . On boiling with strong hydrochloric acid, it is decomposed into carbonic anhydride, ethyl chloride, aldehyde, acetone,

and amonnia. At least four bases can be obtained by the action of dry hydrochloric acid gas on this body.



The original substance unites with bromine to form $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{Br}_4$. When its alcoholic solution is treated with nitrous acid, diethylcollidine dicarboxylate is produced. It is an oily liquid boiling at 310° .

W. C. W.

Dibromopropaldehyde. By E. GRIMAUX and P. ADAM (*Bull. Soc. Chim.*, [2], **36**, 136—139).—On adding 1 mol. bromine to 1 mol. acrolein dissolved in twice its volume of ether, and then expelling the ether, dibromopropaldehyde is obtained as a heavy colourless or slightly yellow liquid, boiling at $79\text{--}85^\circ$ under 5 to 6 mm. pressure. It attacks the eyes and mucous membranes, and reduces Fehling's solution. In contact with air and hydrobromic acid, it undergoes polymerisation, forming a gummy mass, from which crystals may be obtained by distillation under reduced pressure, saturating the distillate with hydrochloric acid gas, and allowing to stand for some days. This compound, when purified by recrystallisation from hot chloroform, presents the same properties as the bromo-compound obtained from metacrolein. Its melting point varies with the rate at which the temperature is raised, since it is depolymerised by heat. When impure, it rapidly alters, and becomes amorphous.

When treated with sodium ethylate, the bromo-derivative yields an oily product, which solidifies, and is obtained by crystallisation from alcohol in small needles (m. p. $77\text{--}78^\circ$) of the same composition as bromacrolein, of which it is probably the polymeride, $\text{C}_9\text{H}_9\text{Br}_3\text{O}_3$; it is neutral and odourless, and without action on Fehling's solution. Sulphuric acid converts it into monobromacrolein.

Monobromacrolein when treated with sodium ethylate at 100° , yields an oil which gives a crystalline body (m. p. 140°) on distillation in steam. It is soluble in water, and gives a white precipitate with ammoniacal silver nitrate, and a yellow with ammoniacal cuprous chloride. It appears to have the composition $\text{C}_9\text{H}_7\text{BrO}_3$, being derived from bromoparacrolein, $\text{C}_9\text{H}_9\text{Br}_3\text{O}_3$, by the elimination of 2HBr , and probably belongs to the propargyl series. It does not act on Fehling's solution. When treated with dilute sulphuric acid it evolves irritating vapours, and yields a solution which reduces Barreswil solution.

L. T. O'S.

Tetrasubstitution Derivatives of Propionic Acid. By H. B. HILL and C. F. MABERY (*Ber.*, **14**, 1679—1682).—Dichloracrylic acid unites with 2 atoms of bromine at 100° , forming α -dichlorodibromopropionic acid, $\text{C}_3\text{H}_2\text{Cl}_2\text{Br}_2\text{O}_2$. This acid dissolves freely in water, ether, or alcohol, but is less soluble in chloroform, benzene, or carbon bisulphide. It crystallises in triclinic prisms (m. p. 95°), the ratio of the axes $a : b : c = 1.034 : 1 : 1.062$. The silver salt crystallises in flat needles. The barium salt forms anhydrous needles, which dissolve freely in water. Both salts are decomposed on heating their solutions.

Dibromacrylic acid at 100° absorbs chlorine and forms β -dichlorodibromopropionic acid. It crystallises in monoclinic prisms (m. p. 119°), which are freely soluble in water, alcohol, or ether, but less soluble in benzene, chloroform, or carbon bisulphide.

The relation between the axes of these crystals is $a : b : c = 2.393 : 1 : 1.731$. The silver salt forms thick needles. The barium salt crystallises in needles containing 2 mols. H_2O : it dissolves freely in water, and the aqueous solution when heated splits up, yielding barium chloride, dibromochlorethylene, and a dibromide, C_2HClBr_4 .

When bromine is added to a solution of dibromacrylic acid in chloroform, *tetrabromopropionic acid* is deposited in triclinic prisms (m. p. 125°).
W. C. W.

Structure of Disubstituted Acrylic Acid. By H. B. HILL (*Ber.*, **14**, 1682—1683).—Dichloracrylic acid from mucochloric acid has the constitution $CCl_2 : CH.CO_2H$. This acid forms monoclinic crystals which are quite distinct from the crystals of the dichloracrylic acid obtained by Wallach from chloralide.
W. C. W.

Dibromacrylic Acid. By H. B. HILL and C. W. ANDREWS (*Ber.*, **14**, 1676—1679).—The dibromacrylic acid obtained by decomposing a solution of tribromopropionic acid in baryta-water with hydrochloric acid, is identical with the acid derived from mucobromic acid. 100 parts of a saturated solution of the pure acid at 18° contain 4.96 parts of the acid.

Barium dibromacrylate crystallises with 1 mol. H_2O . 100 parts of the saturated solution at 18° , contain 5.89 parts of the anhydrous salt. The calcium salt is deposited from a hot aqueous solution in long needles, containing 3 mols. H_2O . The potassium salt forms anhydrous plates.
W. C. W.

Constitution of Glyoxylic Acid. By R. OTTO and H. BECKURTS (*Ber.*, **14**, 1616—1619).—When silver dichloracetate is heated in contact with water, it decomposes into silver chloride, glyoxylic and dichloracetic acids; but if the dry salt is heated at 80° , it splits up into silver chloride, and a mixed anhydride of dichloracetic and glyoxylic acids, $2CH_2Cl.CO_2Ag = 2AgCl + CHCl_2.CO.O.CO.CHO$. The formation of this compound is in favour of the view that glyoxylic acid is *formylcarboxylic acid*, $H.CO.CO_2H$, and not dihydroxyacetic acid.

As a further proof of the correctness of this hypothesis, potassium glyoxylate was subjected to the action of dichloracetic chloride, when potassium chloride, glyoxylic and dichloracetic acids were formed. No anhydride was produced. Hence it appears that potassium glyoxylate is to be regarded as potassium formylcarboxylate containing 1 mol. of water of crystallisation, $C_2HKO_2 + H_2O$, and not as anhydrous potassium dihydroxyacetate.

Dichloracetic chloride is a colourless liquid (b. p. 108°), which fumes strongly in the air. It is decomposed by water, forming dichloracetic acid, and by alcohol forming ethyl dichloracetate. By aqueous ammonia it is converted into an amide (m. p. 96°).

W. C. W

Some Double and Triple Oxalates containing Chromium.

By F. W. CLARKE and E. A. KEBLER (*Amer. Chem. J.*, **3**, 197—201).—*Bariochromic oxalate*, $\text{Cr}_2\text{Ba}_3\text{C}_{12}\text{O}_{24}$, and the corresponding strontium and calcium salts, were discovered in 1845 by Rees-Reece, who obtained them by precipitation from a solution of the ammonium salt, in dark violet silky needles, the barium salt crystallising with 12 and 18 mols. H_2O , the strontium salt with 18, and the calcium salt with $36\text{H}_2\text{O}$.

Kebler, by precipitating from the potassium instead of the ammonium salt, has obtained the *bario-chromic salt* in very dark green silky needles, the amount of water in which varies according to the concentration and temperature of the solutions used. From concentrated solutions, whether cold or hot, a definite hexhydrated salt was obtained; the 12- and 18-hydrated salts of Rees-Reece are doubtless also definite compounds; the salts thrown down from the dilute solutions appear to be mixtures of the hex-hydrated salt with one of these higher hydrates. The sp. gr. of the anhydrous salt was found to be 2.570 at 68° ; that of the 6-hydrate 2.445 at 13.9° ; of the 12-hydrate 2.372 at 27° , the second being nearly a mean between the other two.

The *strontium salts*, prepared under varying conditions of temperature and dilution, also formed pale green satiny needles, easily recrystallisable from hot water; cold dilute solutions yielded the salt, $\text{Cr}_2\text{Sr}_3\text{C}_{12}\text{O}_{24} \cdot 12\text{H}_2\text{O}$, and the mother-liquor and washings deposited a somewhat lower hydrate, possibly a mixture containing $10\frac{1}{2}$ mols. water. Sp. gr. 2.148 at 8.8° . From hot concentrated solutions of the precipitants, a decahydrate was obtained. Clarke thinks it probable that all these lower hydrates are mixtures of a 12-hydrated salt with a hexhydrate yet to be discovered.

The mother-liquors of all these strontium precipitates, when united, concentrated, and left at rest, deposited a very dark green, almost black, crystalline crust, consisting of a triple oxalate, $\text{Cr}_2\text{Sr}_2\text{K}_2\text{C}_{12}\text{O}_{24}$, with 11 or 12 mols. H_2O . Clarke regards the 12 mol. formula as the true one.

The corresponding *barium salt*, $\text{Cr}_2\text{Ba}_2\text{K}_2\text{C}_{12}\text{O}_{24}$, was obtained by mixing equivalent quantities of bario-chromic and potassio-chromic oxalates dissolved in boiling water, and separated in bluish-green needles containing 5 or 6 mols. H_2O , most probably the latter.

H. W.

Decomposition of Calcium Succinate by Heat. By A. FUNARO (*Gazzetta*, 1881, 274—277).—D'Arcet, by subjecting this salt to dry distillation, obtained a brown aromatic liquid, which he called *succinone*, but its percentage composition differed widely from that of the ketone of succinic acid (*Ann. Chim. Phys.* [2], **58**, 297). More recently Richter (*Bull. Soc. Chim.* [2], **35**, 122) endeavoured to prepare the same ketone, but obtained nothing but a mixture of ill-defined volatile bodies, which when distilled over zinc yielded benzene. The author of the present paper has obtained, by the dry distillation of calcium succinate, a small quantity of yellow-brown oily empyreumatic liquid, separable by fractional distillation into several portions, viz. : (1.) A small quantity of liquid distilling just above 60° , having the

odour of acetone, and crystallising with alkaline bisulphites: its quantity was not sufficient for the determination of its boiling point. (2.) Between 115° and 125° , a yellow fragrant liquid, having the composition and physical properties of *heptylidene*, C_7H_{12} .

The higher fractions are difficult to separate, as they do not differ much in boiling point. (3.) Between 180° and 188° , a greenish neutral liquid insoluble in water, soluble in alcohol, and having an odour characteristic of phenol. Mean of three analyses: $C = 77.92$; $H = 8.11$ per cent. (4.) Between 190° and 200° : a relatively large quantity of liquid, greenish when recently distilled, afterwards turning yellowish-brown, and likewise having the odour of phenol. Mean of analyses: $C = 79.52$; $H = 8.58$, agreeing nearly with the formula $C_9H_{12}O$. (5.) Between 205° and 212° : greenish-yellow liquid, having a faint odour and the composition $C = 80.98$, $H = 9.40$ per cent. (6.) Between 215° and 225° : dark-green; difficult to separate from the preceding; neutral, and has a faint odour. $C = 81.20$. $H = 9.20$. (7.) Between 230° and 280° . Dense brown liquids, having an aromatic odour, but exhibiting no characteristic properties, and impossible to purify.

The centesimal composition and physical properties of all these bodies tend to show that they may with some probability be regarded as allied to the phenols and aromatic ketones: thus the fraction boiling at 180 – 188° bears some resemblance to *cresol*; and that which boils at 215 – 225° is similar in composition and properties to *phenylisobutyl ketone*. The quantities of these bodies obtained were too small to admit of an examination of their products of oxidation.

H. W.

Derivatives of Itaconic, Mesaconic, and Citraconic Acids.

By W. PETRI (*Ber.*, **14**, 1634–1637).—*Ethyl itaconate* boils at 228° , *ethyl citraconate* at 231° , and *ethyl mesaconate* at 229° . On saponification with baryta-water, these ethereal salts yield the corresponding barium salts, which crystallise with 1, $2\frac{1}{2}$, and 4 mols. H_2O respectively. Barium mesaconate is the most soluble of the three salts.

Itaconic chloride, $C_3H_4(COCl)_2$, is a colourless liquid boiling at 89° under a pressure of 17 mm. Under the same pressure *mesaconic chloride* boils at 80° . These chlorides are converted into the corresponding acids by contact with water. By the action of phosphorous pentachloride on citraconic anhydride, mesaconic chloride appears to be formed.

Mesaconic acid is converted into citraconic anhydride, by the action of acetic chloride at 100° in sealed tubes.

Isodibromopyrroacemic anhydride is obtained in rhombic crystals (m. p. 50°) by the addition of bromine to a solution of itaconic anhydride in chloroform. On distillation, it splits up into hydrobromic acid and bromitaconic anhydride.

W. C. W.

Pyrroacemic Acid Compounds. By C. BÖTTINGER (*Ber.*, **14**, 1599–1600).—Combination ensues when benzonitril is added to a cold solution of pyrroacemic acid in concentrated sulphuric acid. By pouring the mixture on to ice, the addition-product $C_{17}H_{16}N_2O_4$ is obtained in the form of a white crystalline substance, which dissolves

sparingly in benzene, chloroform, and ether, and freely in acetone. This substance crystallises in colourless four-sided plates, which melt at 172° with decomposition. It acts as an acid and has an exceedingly bitter taste. When boiled with strong potash-solution it splits up, forming ammonia and benzoic acid.

A similar compound, having the composition $C_{19}H_{20}N_2O_4$ is obtained by the action of benzyl cyanide on pyrrocemic acid in presence of strong sulphuric acid.

This substance melts at 145° .

W. C. W.

Acids of the Australian Currant, *Leptomeria acida*. By E. H. RENNIE (*J. Roy. Soc., N.S.W.*, **14**, 119—121).—The intensely sour taste of this fruit is due chiefly to malic acid, which is present in the solid residue obtained by just neutralising the juice with sodium carbonate and evaporating to dryness, to the amount of more than 40 per cent. Small quantities of tartaric and citric acids are also present. The ash contains a considerable quantity of potassium carbonate with a mere trace of calcium carbonate.

H. W.

Carbogluconic Acid. By P. SCHÜTZENBERGER (*Bull. Soc. Chim.* [2], **36**, 144).—When inverted sugar is heated with hydrocyanic acid at 100° in a close vessel for some hours, ammonium carbogluconate, $C_7H_{13}O_8.NH_4$, is formed. Glucose and cane-sugar behave in the same way, but the reaction is slower with the latter. The free acid, $C_7H_{14}O_8$, is colourless, amorphous, and very soluble in water, and of slightly acid taste. Its alkaline salts, which are very soluble in water, give a white precipitate with lead acetate. They are optically inactive, and do not reduce Fehling's solution.

By leaving inverted sugar in contact with hydrocyanic acid in the cold until the colour begins to change to brown, and expelling the excess of hydrocyanic acid, a solution is obtained which reduces Fehling's solution at the ordinary temperature.

L. T. O'S.

Barbituric Acid. By M. CONRAD and M. GUTHZEIT (*Ber.*, **14**, 1643—1645).—*Dimethylbarbituric acid*, prepared by the action of methyl iodide on silver barbiturate, crystallises in glistening plates, which sublime without melting at 200° . On decomposition by boiling with potassium hydroxide, dimethylmalonic acid (m. p. 185°) is formed. On the addition of silver nitrate to a neutral solution of dimethylbarbituric acid, two atoms of silver replace the hydrogen atoms which are combined with the nitrogen atoms.

W. C. W.

Decomposition of Potassium Picrate. By SARRAU and VIEILLE (*Compt. rend.*, **93**, 61—62).—The volume and percentage composition of the gas produced by the explosion of potassium picrate in a closed vessel under varying conditions of pressure are given in the following table:—

Mean density of products	0.023	0.3	0.5
Volume of gas per kilo. at 0° , 760 mm.	574.1	557.9	—

Hydrocyanic acid (ammonium cyanide)	1·98	0·32	0·31
Carbonic anhydride.....	10·56	13·37	20·48
Carbonic oxide.....	62·10	59·42	50·88
Methane	0·17	2·38	5·39
Hydrogen.....	10·31	6·77	2·68
Nitrogen	16·88	17·74	18·26

With increased pressure, the proportion of carbonic oxide and free hydrogen diminishes, whilst that of carbonic anhydride and methane increases. The composition of the solid residue also varies with the pressure. It consists of potassium carbonate and cyanide with a small quantity of free carbon, amounting under high pressures to about 0·1 per cent. The proportion of potassium converted into cyanide under different pressures is as follows:—

Density.....	0·23	0·3	0·5
Potassium converted into cyanide, per cent.	29·8	34·7	24·3
Appearance of residue .	slightly carbonaceous	white	carbonaceous

With a density of 0·5 the decomposition may be approximately represented by the equation* $8\text{C}_{12}\text{H}_2\text{K}(\text{NO}_4)_3\text{O}_2 = 2\text{KC}_y + 6\text{KCO}_3 + 21\text{CO}_2 + 52\text{CO} + 22\text{N} + 3\text{C}_2\text{H}_4 + 4\text{H} + 7\text{C}$, with a tendency to the replacement of the three last terms by $4\text{C}_2\text{H}_4 + 5\text{C}$.

C. H. B.

Methyldeoxybenzoin. By W. MANN (*Ber.*, **14**, 1645—1647).—The phenylacetic acid used in the preparation of methyldeoxybenzoin was obtained by the following process:—100 grams of benzyl chloride dissolved in 100 grams of alcohol are gradually added to a solution of 60 grams of pure potassium cyanide (which must be free from cyanate) in 55 grams of water, which is contained in a flask provided with an upright condenser. After heating the mixture for three hours, the upper layer of liquid is decanted and distilled. The portion boiling below 236° is heated with 45 grams of potassium hydroxide dissolved in 25 grams of water, in a flask fitted with an upright condenser, for five or six hours until the evolution of ammonia ceases. The alcohol is then distilled off, water is added, and the mixture filtered. The phenylacetic acid is precipitated from the filtrate by hydrochloric acid.

Paramethyldeoxybenzoin, $\text{CH}_2\text{Ph}.\text{CO}.\text{C}_6\text{H}_4\text{Me}$, prepared by the action of phenylacetic chloride on toluene in the presence of aluminium chloride, crystallises in white plates (m. p. $107\cdot5^\circ$), which dissolve in alcohol, ether, chloroform, and benzene. It boils without decomposition above 360° . On oxidation with nitric acid, it yields a mixture of paratoluic and terephthalic acids, and on reduction with phosphorus and hydriodic acid, it is converted into paramethyldibenzyl,



This substance melts at 27° and boils at 286° . It is soluble in alcohol, ether, chloroform, and benzene.

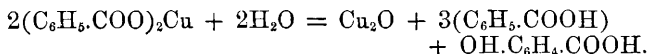
* O = 8.

Paratolyl-benzyl carbinol, $\text{CH}_2\text{Ph}.\text{CH}(\text{OH}).\text{C}_6\text{H}_4\text{Me}$, obtained by the action of sodium and alcohol on methyldeoxybenzoin, crystallises in small needles, soluble in alcohol, ether, and benzene. It melts at 66° , and boils above 360° .

An acid, $\text{C}_{19}\text{H}_{20}\text{O}_2$, is also obtained as a bye-product in the preparation of the alcohol. It crystallises in thin white needles (m. p. 92.5°), soluble in alcohol, ether, benzene, and chloroform.

Methylstilbene, $\text{CHPh}:\text{CH}.\text{C}_6\text{H}_4\text{Me}$, is formed when paratolyl-benzyl carbinol is boiled with dilute sulphuric acid (1 : 4). It crystallises in pearly plates, soluble in ether, benzene, and chloroform. This hydrocarbon melts at 117° , and boils without decomposition at a higher temperature. W. C. W.

Synthesis of Salicylic Acid. By E. F. SMITH (*Amer. Chem. J.*, 2, 338).—When 1 part of copper benzoate is heated with about 3 parts of water in a sealed tube at 180° for three hours, a large quantity of cuprous oxide separates; and on acidulating the liquid with hydrochloric acid, and supersaturating with hydrogen sulphide, the filtrate from the copper sulphide contains a large quantity of benzoic acid, which may be removed by distillation with steam; whilst the residual liquid, when evaporated to a small bulk, yields a crop of needle-shaped crystals melting at 156° , and giving with ferric chloride the coloration characteristic of salicylic acid. The reaction is represented by the equation—



The same result is obtained by heating aqueous benzoic acid with an ammoniacal solution of cupric oxide at 220° . H. W.

Introduction of Aromatic Hydrocarbons into Ketonic and Aldehydic Acids. By C. BÖTTINGER (*Ber.*, 14, 1595—1598).— *α -Diphenylpropionic acid* is formed by the action of benzene on pyroracemic acid in presence of sulphuric acid. Pyroracemic acid is carefully dissolved in ten times its volume of concentrated sulphuric acid, which is cooled down to -10° in a freezing mixture. Benzene is added to the solution, and the liquid is taken out of the freezing mixture, but the temperature is not allowed to reach $+10^\circ$. When the reaction is complete, the product is poured into cold water, and the liquid which separates on the surface of the water is exposed to a current of air; the benzene evaporates and leaves crystals of *α -diphenylpropionic acid*, which is identical with the diphenylmethylacetic acid of Thörner and Zincke (*Abstr.*, 1879, 322).

By a similar reaction *α -ditolylpropionic acid* can be prepared from pyroracemic acid and toluene. On recrystallisation from ether or alcohol, this acid is obtained in monoclinic cubes (m. p. 151°).

α -Diethylphenylpropionic acid prepared from pyroracemic acid and ethylbenzene is deposited from a solution in dry ether in four-sided transparent plates (m. p. 116°). The acid is freely soluble in chloroform and in light petroleum.

Dibromopyroracemic acid combines readily with toluene in the

presence of strong sulphuric acid, forming methyl dibromatrolactic acid (m. p. 163°). This acid crystallises from an ethereal solution in thick prisms, and from chloroform in slender needles. It is decomposed by warm water into carbonic anhydride and methylacetophenone bromide (m. p. 55°). The bromide is deposited from an aqueous solution in plates, and from an ethereal solution in long needles. By the action of sodium amalgam it is converted into *methylatrolactic acid*, which crystallises in transparent four-sided plates, soluble in water and in chloroform.

W. C. W.

Vulpic Acid. Part III. By A. SPIEGEL (*Ber.*, **14**, 1686—1696).—Vulpic acid is not attacked by ammonia, but it is saponified by the action of lime, forming methyl alcohol and pulvic acid, $C_{19}H_{14}O_5 + H_2O = C_{18}H_{12}O_5 + CH_4O$. Pulvic acid is decomposed by potassium or sodium hydroxide into dibenzylglycollic acid: $C_{18}H_{12}O_5 + 2H_2O = C_{16}H_{16}O_3 + 2CO_2$, and by baryta-water it is split up into phenylacetic and oxalic acids: $C_{18}H_{12}O_5 + 3H_2O = 2C_6H_8O_2 + C_2H_2O_4$.

Dibenzylglycollic acid has already been shown to be identical with the oxytolylglycollic acid of Möller and Strecker. The amide of this acid is obtained by the action of hydrochloric acid on dibenzylketone cyanhydrin at 120—130°. It is deposited from a solution in benzene in long colourless needles (m. p. 193°), insoluble in ether. It is converted into dibenzylglycollic acid by treatment with hydrochloric acid at 140°.

The acetic derivative of this acid is obtained in the pure state by distilling off the excess of acetic anhydride from the crude product of the action of acetic anhydride on dibenzylglycollic acid. The residue is dissolved in a hot solution of sodium hydroxide, and, on cooling, the sodium salt is obtained in pearly plates. The free acid crystallises in plates (m. p. 106°), soluble in chloroform and in light petroleum. When heated to 190—200°, the acetic derivative decomposes into acetic acid and dibenzylglycollic anhydride, which crystallises in small prisms (m. p. 157°), soluble in alcohol, ether, chloroform, hot benzene, and carbon bisulphide. It dissolves in a cold solution of sodium hydroxide, forming sodium dibenzylglycollate.

Oxidation and Reduction of Pulvic Acid.—Pulvic acid is oxidised by potassium permanganate in alkaline solution, yielding oxalic and phenylglyoxylic acids. When ammoniacal solution of pulvic acid is boiled with zinc-dust, ammonium carbonate escapes, and a new acid is formed, to which the name *hydrocornicularic*, $C_{17}H_{16}O_3$, has been given, together with several non-crystalline compounds. The mixture is separated by fractional precipitation, the first portion of the precipitate containing the acid; this is treated with hydrochloric acid to remove zinc, and recrystallised from alcohol. In this way it is obtained in colourless needles or prisms (m. p. 134°), which dissolve freely in ether, chloroform, benzene, and glacial acetic acid. Hydrocornicularic acid is monobasic. The salts of the potassium and calcium groups are non-crystalline. The lead and silver salts are amorphous and insoluble. The methyl salt, which is formed by the reduction of the vulpic acid, crystallises in monoclinic prisms (m. p. 68°). The anhydride, $C_{17}H_{14}O_2$, is decomposed by heat into water and an inner anhydride, which crystallises in colourless needles (m. p. 117°),

soluble in ether, chloroform, benzene, glacial acetic acid, hot alcohol, and carbon bisulphide. The anhydride is converted into sodium hydrocornicularate by boiling its alcoholic solution with soda.

Tetrahydrocornicularic acid, $C_{17}H_{18}O_3$, is formed by the action of sodium amalgam on an aqueous solution of hydrocornicularic acid. It is a thick oily liquid, and is converted into the anhydride $C_{17}H_{16}O_2$ by boiling with water. The anhydride forms thin needles or plates (m. p. 70°), soluble in alcohol, ether, chloroform, and benzene. It is always produced in small quantities in the preparation of hydrocornicularic acid from pulvic acid.

By fusion with potassium hydroxide, hydrocornicularic acid is split up into toluene and phenylsuccinic acid, $C_{10}H_{10}O_4$, which crystallises in short needles (m. p. 167°), soluble in alcohol, ether, and glacial acetic acid. The lead and silver phenylsuccinates are insoluble. The calcium salt precipitated from a cold solution contains 2 mols. H_2O , but it is anhydrous when prepared from a boiling solution. The acid is identical with the phenylsuccinic acid obtained synthetically by the author, and also by L. Rügheimer (*Ber.*, **14**, 428).

Hydrocornicularic acid may be regarded as a diphenylhydroxyangelic acid, and tetrahydrocornicularic acid as a diphenylhydroxyvalerianic acid having the constitution $COOH.CHPh.CH_2.CH(OH).CH_2Ph$.

W. C. W.

Metachloronitro- and Metachloramido-benzenesulphonic Acids. By J. POST and C. G. MEYER (*Ber.*, **14**, 1605—1607).—Metachloronitrobenzene yields two sulphonic acids, which are easily distinguished by the properties of their salts.

α -Metachloronitrobenzenesulphonic Acid.

$[C_6H_3(NO_2)Cl.SO_3]_2Ba + 2H_2O$, small yellowish-brown plates or needles, freely soluble in alcohol.

$[C_6H_3(NO_2)Cl.SO_3]_2Sr + \frac{1}{2}H_2O$, brown plates, soluble in alcohol.

$C_6H_3(NO_2)Cl.SO_3K$, small needles or plates, freely soluble in alcohol.

$C_6H_3(NO_2)Cl.SO_3Na + 2\frac{1}{2}H_2O$, pale yellow needles, arranged in groups, and efflorescent.

β -Metachloronitrobenzenesulphonic Acid.

$[C_6H_3(NO_2)Cl.SO_3]_2Ba + \frac{1}{2}H_2O$, small yellow needles, insoluble in alcohol.

$[C_6H_3(NO_2)Cl.SO_3]_2Sr$, yellow crystalline powder, soluble in alcohol.

$C_6H_3(NO_2)Cl.SO_3K + \frac{1}{2}H_2O$, pale yellow prisms.

These acids yield the corresponding amidobenzenesulphonic acids on reduction.

α .

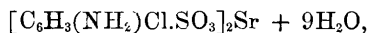
$C_6H_3(NH_2)Cl.SO_3H$, colourless silky needles, soluble in hot water.

β .

$C_6H_3(NH_2)Cl.SO_3H$, brown plates, sparingly soluble in water.

$[C_6H_3(NH_2)Cl.SO_3]_2Ba + 7\frac{1}{2}H_2O$, thick colourless needles, soluble in water and in alcohol.

Metachloramidobenzene appears to yield only one monosulphonic acid when acted on by sulphuric acid, $\text{C}_6\text{H}_3(\text{NH}_2)\text{Cl}.\text{SO}_3\text{H}$, red crystals, sparingly soluble in water. $[\text{C}_6\text{H}_3(\text{NH}_2)\text{Cl}.\text{SO}_3]_2\text{Ba} + \text{H}_2\text{O}$, small yellow efflorescent needles soluble in alcohol.

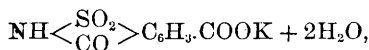


long colourless efflorescent needles, freely soluble in alcohol and in water. $\text{C}_6\text{H}_3(\text{NH}_2)\text{Cl}.\text{SO}_3\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, pale yellow glistening needles. $\text{C}_6\text{H}_3(\text{NH}_2)\text{Cl}.\text{SO}_3\text{Na} + 2\text{H}_2\text{O}$, colourless needles which lose water at 100° .
W. C. W.

Oxidation of Sulphaminemetatoluic Acid in Alkaline and in Acid Solution. By R. D. COALE and I. REMSEN (*Amer. Chem. J.*, **3**, 204—216).—Remsen and Hall have shown that sulphamine-paratoluic acid is converted, by oxidation with permanganate in alkaline solution, into anhydrosulphamine-terephthalic acid, or terephthalic sulphinide, whereas when the oxidation takes place in an acid solution the product consists of sulphoterephthalic acid (this volume, p. 819). In the present paper it is shown that similar transformations take place in the meta-series. Free sulphamine-metatoluic acid oxidised with potassium permanganate yields pure *sulpho-isophthalic acid*.

$\text{C}_6\text{H}_3(\text{SO}_3\text{H})(\text{COOH})(\text{COOH})$, identical with that which is obtained by oxidation of metaxylenesulphonic acid. Sulpho-isophthalic acid prepared by either of these processes, and purified by conversion into barium salt, &c., is very easily soluble in water and hygroscopic, and may be obtained, by evaporation over sulphuric acid, as a semi-crystalline mass melting at $243\text{--}244^\circ$. Its salts are more or less unstable, and have not been obtained of uniform composition. The tripotassic salt, $\text{C}_6\text{H}_3\text{K}_3\text{SO}_7$, is very soluble in water and uncrystallisable.

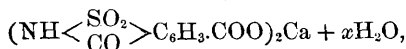
When an alkali is added to the oxidising mixture, the sulphamine-metatoluic acid is converted—like the corresponding acid in the para-series—into *anhydrosulphamine-isophthalic acid* or *isophthalic sulphinide*, $\text{NH} < \begin{smallmatrix} \text{SO}_2 \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_3.\text{COOH}$, which may be separated from the liquid in the same manner as the corresponding para-compound (p. 819). It crystallises well, and melts at 282.5° . Its *monopotassium salt*,



prepared by adding the calculated quantity of potassium carbonate to the aqueous solution of the sulphinide, crystallises in well-formed transparent rectangular prisms, which give off their water at $110\text{--}120^\circ$.

Normal potassium sulphamine-isophthalate, $\text{NH}_2.\text{SO}_2.\text{C}_6\text{H}_3(\text{COOK})_2$, prepared by neutralising the solution of the preceding salt, crystallises in long needles.

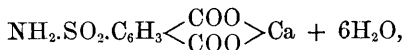
Acid calcium anhydrosulphamine-isophthalate,



prepared by neutralising one-half of a solution of the anhydro-acid or

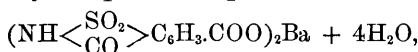
sulphinide, and then adding the other half, separates on evaporation to a small bulk, partly amorphous, partly in feathery crystalline masses, which quickly lose their water. The air-dried salt contains 4 mols. H_2O , which are given off at 130° .

Calcium sulphamine-isophthalate,



is obtained by boiling a solution of the acid with powdered Iceland spar, and separates on evaporation to a small bulk in large finely developed crystals, apparently monoclinic: on exposure to the air, they quickly give off half their water and crumble to an amorphous powder; the remaining half of the water is given off at 170 – 180° .

Acid barium anhydrosulphamine-isophthalate,



obtained by boiling the acid potassium salt with barium chloride, crystallises in well-formed transparent monoclinic plates, which lose their water at 100 – 105° .

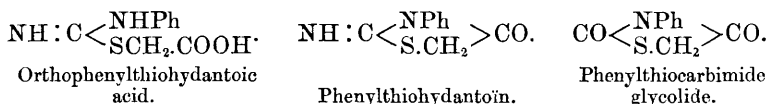
Barium sulphamine-isophthalate, $\text{NH}_2.\text{SO}_2.\text{C}_6\text{H}_3 < \begin{smallmatrix} \text{COO} \\ \text{COO} \end{smallmatrix} > \text{Ba} + 4\text{H}_2\text{O}$,

prepared by boiling the acid with barium carbonate in a large quantity of water, forms thick monoclinic plates, which on exposure to the air lose part of their water and fall to pieces. Its solution when boiled deposits a white powder, apparently in consequence of decomposition.

H. W.

A New Phenylthiohydantoic Acid. By P. J. MEYER (*Ber.*, **14**, 1659—1664).—*Orthophenylthiohydantoic acid* is deposited in microscopic needles on heating an alcoholic solution of phenylthiocarbamide and ammonium monochloracetate. It is isomeric with the phenylcarbodi-imidothiacetic acid which Jäger (*J. pr. Chem.*, 1877, 16) obtained from aniline, monochloracetic acid, and ammonium thiocyanate. On heating, it decomposes without melting. By boiling with glacial acetic acid or strong ammonia, it is converted into orthophenylthiohydantoïn, which is deposited in prisms (m. p. 178°) when the solution is neutralised. If dilute hydrochloric acid is substituted for the glacial acetic acid, phenylthiocarbimide glycolide is produced. The properties of this substance have been described by Lange (*Ber.*, **12**, 597).

The author represents the constitution of these compounds by the following formulæ:—



Orthophenylthiohydantoic acid.

Phenylthiohydantoïn.

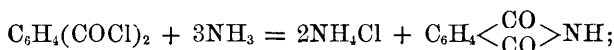
Phenylthiocarbimide glycolide.

W. C. W.

Phthalimide. By M. KUHARA (*Amer. Chem. J.*, **3**, 26—30).—By dissolving phthalic chloride in aqueous ammonia, and treating the solution with hydrochloric acid, the author (in one experiment only)

obtained, together with other products, rhombohedral crystals having the composition of phthalimide, $C_8H_5NO_2$, but differing in properties from the normal phthalimide, $C_6H_4<\overset{CO}{CO}>NH$, obtained by the action of heat on phthalate or phthalamate of ammonium, or by fusing phthalic anhydride with urea, inasmuch as they melted at 192° and were soluble in cold, more readily in hot water and alcohol, whereas normal phthalimide melts at 230° and is insoluble in cold water and alcohol. Now as phthalic chloride—prepared by the action of PCl_5 on phthalic acid at the boiling heat—has been shown by v. Gerichten (this Journal, 1880, Abstr., 473) to consist either wholly of the compound $C_6H_4<\overset{CCl_2}{CO}>O$, or of a mixture of this with the normal chloride, $C_6H_4(COCl)_2$, the author infers that the isomeric phthalimide prepared from it has the constitution $C_6H_4<\overset{C(NH)}{CO}>O$.

Phthalic chloride treated with gaseous ammonia is converted directly into normal phthalimide, a reaction which would be most simply represented by the equation—



but as the chloride has been shown to consist wholly or chiefly of $C_6H_4<\overset{Cl_2}{CO}>O$, it may be supposed that the isomeric phthalimide is formed in the first instance, and then changes spontaneously into the normal imide.

Phthalimide, boiled in aqueous solution with excess of baryta-water, is converted into *barium phthalamate* $(C_6H_4<\overset{CONH_2}{CO}>)_2Ba$, which is precipitated from the resulting solution by alcohol as an amorphous powder. The *potassium salt*, prepared from it by double decomposition, crystallises in thin, transparent, silky needles, easily soluble in water and in alcohol. The *copper salt* is an amorphous powder.

H. W.

Cork-tar. By L. BONDET (*Compt. rend.*, 92, 728).—In the production of illuminating gas from cork, a certain amount of liquid distillate is obtained. This separates into two layers, the upper consisting of water containing in solution acetic acid (with propionic and higher homologues), ammonia, and a small quantity of methylamine, hydrocyanic acid, and methyl alcohol.

The lower layer is a dark-brown very fluid tar, which may be separated by distillation into three portions. The first portion (27 per cent. of the tar) boiling below 210° , contains a large quantity of naphthalene, benzene (4 per cent. of the tar), and toluene (3 per cent. of the tar). Sodium hydroxide and sulphuric acid abstract little or nothing from this portion of the tar.

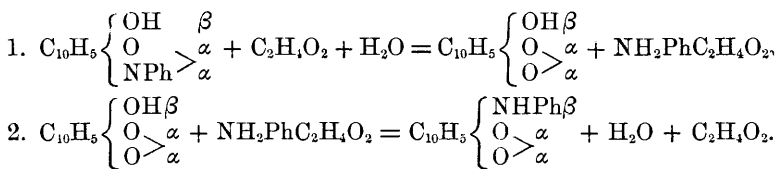
The heavy oil boiling above 210° also contains but small quantities of phenols. The highest boiling portions of the tar contain a large quantity of anthracene.

C. W. W.

Action of Aluminium Chloride on a Mixture of Naphthalene and Ethyl Chloride. By C. MARCHETTI (*Gazzetta*, **11**, 265—267).—By treating this mixture with sublimed aluminium chloride, according to the method of Friedel and Crafts, in a flask containing a small quantity of dry hydrochloric acid gas, and connected with a reflux apparatus, the author obtained a mixture of hydrocarbons, partly solidifying at ordinary temperatures, partly at 0° , while the rest remained liquid at -10° ; and on redistilling the portion which remained liquid at 0° in a Sprengel vacuum at 5—6 mm. pressure, he obtained between 114° and 116° , a colourless distillate intermediate in composition between *mono-* and *di-ethylnaphthalene*, and yielding a picrate which crystallised in thin yellow needles melting at 70° . The action of bromine on this mixture did not yield any definite products.
H. W.

Naphthaquinone. By O. MILLER (*Ber.*, **14**, 1600—1602).—By the action of a solution of chromic acid in glacial acetic acid on a solution of the acetic derivative of α -naphthol in the same solvent, a mixture of naphthaquinones is produced, from which three products can be separated by distillation in a current of steam, and by crystallisation from spirits of naphtha. The most volatile portion crystallises in orange-coloured needles (m. p. 120°); the second portion forms thick needles or prisms of a deep orange colour (m. p. 119°); the less volatile portion crystallises in long needles (m. p. 113°) of a dark orange colour. α -Naphthol on oxidation with an acetic acid solution of chromic acid yields small quantities of ordinary naphthaquinone (m. p. 124°) and a complicated substance, which is not volatile in a current of steam.
W. C. W.

Conversion of β -Naphthaquinoneanilide into α -Naphthaquinoneanilide By C. LIEBERMANN (*Ber.*, **14**, 1664—1667).—Zincke's observation (*Ber.*, **14**, 1494) that β -naphthaquinoneanilide is converted into the α modification by boiling with sulphuric acid and alcohol, or by the action of glacial acetic acid at 140° , can be easily explained on the assumption that the anilide splits up into α -hydroxynaphthaquinone and an aniline salt, and that the aniline salt acts on the hydroxyl-group of the hydroxynaphthaquinone forming α -naphthaquinoneanilide.



W. C. W.

Cyano-camphor. By A. HALLER (*Compt. rend.*, **93**, 72—74).—When heated with concentrated hydrochloric acid in a closed tube at 100° , cyano-camphor yields ammonium chloride and campho-carboxylic acid, but at the temperature of the reaction, the latter splits up into camphor and carbonic anhydride. Cyano-camphor, in alcoholic solution, gradually decomposes with formation of hydrocyanic acid and camphic acid, $\text{C}_{10}\text{H}_{16}\text{O}_2$. The same decomposition takes place when a

small quantity of potassium hydroxide is added to the alcoholic solution. When oxidised with potassium permanganate in neutral or alkaline solution, or with chromic mixture, cyano-camphor yields hydrocyanic acid and camphoric acid, $C_{10}H_{16}O_4$. This property of readily giving up hydrocyanic acid is apparently common to all the substitution derivatives of cyano-camphor.

C. H. B.

Colouring Matter from Beth-a-barra Wood. By S. P. SADTLER and W. L. ROWLAND (*Amer. Chem. J.*, **3**, 22—26).—This wood, recently imported into America from the West Coast of Africa, is much valued for its extreme toughness, and its capability of receiving a high polish. Its colour is very much like that of ordinary black walnut, but on close examination the interstices of the fibres are seen to be filled with a yellow crystalline substance, just as those of rhubarb and araroba roots are filled with chrysophanic acid. The colouring matter may be extracted from the shavings, or better from the sawdust and raspings of the wood, by heating with distilled water containing a little sodium carbonate, and is precipitated from the resulting claret-coloured solution by acetic acid in flocks, and purified by repeated crystallisation from hot alcohol of 80 per cent. As thus prepared, it is a tasteless yellow compound, crystallising in scales or needles, which under the microscope appear to be made up of flat prisms laterally joined. It is not altered by contact with the air, whether dry or moist; dissolves very readily in alcohol and in ether; very slightly in pure water even when hot; but easily on addition of a trace of alkali or alkaline carbonate.

From chrysophanic acid, which it somewhat resembles in appearance, the Beth-a-barra colour is distinguished by the following characters and reactions. *Chrysophanic acid* melts at 162° , and forms with ammonia and the fixed alkalis deep red solutions, from which it is precipitated on neutralisation. Sodium hydroxide extracts the colour from solutions of chrysophanic acid in ether, chloroform, benzene, or light petroleum, yielding deep-red solutions; ammonia extracts the colour from solutions in ether or light petroleum, but not from solution in chloroform or benzene. An ammoniacal solution of chrysophanic acid is precipitated lilac by lead acetate, and rose-coloured by alum. The *Beth-a-barra colour* melts at 135° , and forms solutions with alkalis like those of chrysophanic acid. Sodium hydroxide and ammonia both extract the colour from solutions in ether, benzene, light petroleum, and chloroform. An ammoniacal solution is precipitated brick-red by lead acetate, and no compound appears to be formed in alum solutions. Chrysophanic acid ignited with zinc-dust yields methylanthracene; the Beth-a-barra colour when similarly treated yields phenol-like bodies, smelling like wood-tar creasote, and dissolving in alkalis with violet colour. Lastly, the Beth-a-barra colour, dried at 125° , gives by analysis 75.41 per cent. carbon, and 6.54 hydrogen, agreeing nearly with the empirical formula $C_{28}H_{29}O_{51}$, or possibly $C_{22}H_{23}O_4$, and at 100° it gives 68.77 C. and 6.05 O, agreeing with $C_{28}H_{29}O_5 + 3H_2O$, whereas chrysophanic acid (dihydroxymethylanthraquinone) contains 70.87 per cent. C and 3.94 H, and is represented by the formula $C_{15}H_{10}O_4$.

The Beth-a-barra colour also differs from *chrysarobin*, the chief constituent of goa-powder (from araroba root), which contains 72.29 per

cent. carbon and 5.22 hydrogen; dissolves in strong potash-solution with yellow colour and green fluorescence; and when heated with the same solution in contact with the air is converted into chrysophanic acid.

H. W.

Studies on the Quinoline Series. By J. DEWAR (*Proc. Roy. Soc.*, **30**, 164—169).—The author has already shown (this Journal, 1877, **2**, 299) that the leucoline bases occurring in coal-tar are aromatic derivatives, inasmuch as when oxidised by potassium permanganate, they are converted into leucolinic acid, $C_9H_5NO_3$, which, when decomposed by distillation with an alkali, yields aniline; and this conclusion has been confirmed by the synthesis of quinoline from hydrocarbostyryl (Baeyer, *ibid.*, 1879, Abstr., 946), and from allylaniline (Königs, *ibid.*, 540). By further oxidation with permanganate, the same bases are converted into pyridine-dicarboxylic acid, $C_5H_3N(COOH)_2$ (*ibid.*, 1879, Abstr., 1731; 1880, 405, 895).

In the present paper, it is shown that quinoline (C_9H_7N) obtained from cinchonine is converted by oxidation with permanganate in acid solution into quinolinic acid, an acid isomeric with leucolinic acid, but melting at 143° , *i.e.*, 20° lower than the latter. It crystallises in nodular masses very soluble in water. Its silver salt is very sparingly soluble, and separates from cold solutions as a flocculent precipitate, which becomes crystalline on standing. By recrystallisation from a large volume of boiling water, this salt is obtained in tufts of slender needles, always however mixed with a brown substance, apparently silver oxide. The acid gives no colour with ferric chloride, but the ammonia salt gives a violet precipitate, quickly changing to reddish-brown.

The acid fused with potassium hydroxide gives aniline, and the silver salt when heated yields a crystalline sublimate, together with drops of aniline. The acid dissolves in hot glycerol, with fine violet fluorescence, and begins to decompose, giving off carbonic anhydride at 180° , together with drops of aniline.—*Leucolinic acid* does not decompose in glycerol below 205° : its general decompositions are identical with those of quinolinic acid, and prove conclusively that both these acids belong to the aromatic group.

Tar Leucoline.—According to Greville Williams, the leucoline of tar is distinguished from the corresponding cinchona-base by forming an oily uncrystallisable chromate. Dewar, on the other hand, finds that the leucoline used in his own experiments was a mixture of two isomeric bases, one of which yielded a crystallised chromate, not however identical with the chromate of the alkaloid base. The largest yield of crystalline chromate was obtained from the portion of the base which boiled between 210° and 220° . In no case did the mixture of the base with excess of chromic acid yield crystals until it had stood for several days. After separating the crystals, the free base was obtained by distillation with potassium hydroxide, and immediately gave a well-crystallised salt on addition of a little chromic acid. The existence of at least two distinct leucolines in tar is also shown by the reaction of crude leucoline with chloride and iodide of ethyl, whereby two ethylated bases are formed, distinguished from one another by their behaviour to chromic acid.

Oxidation of Leucoline.—The largest amount of leucolinic acid is obtained when 1 part of the base dissolved in the form of sulphate is treated with $2\frac{1}{2}$ parts of potassium permanganate dissolved in boiling water. The crude acid separated from the potassium or lead salt always contains a considerable quantity of a syrupy acid, perhaps derived from one of the isomeric bases, which does not crystallise unless it is boiled with water for some days.

Crystalline leucolinic acid treated with glycerol gives a small quantity of substance exhibiting the reactions characteristic of indole. If fused lead chloride be used instead of glycerol, the distillate consists of aniline hydrochloride without any of the indole substance. Similarly a solution of the potassium salt of the acid heated to 200° , gave only aniline, carbonic acid, and acetic acid. On heating the acid with zinc-dust, quinoline was not reproduced, the product consisting of a crystalline substance not yet examined.

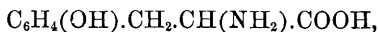
Leucolinic and quinolinic acids appear from their decompositions to consist of *amidophenylpyruvic acids*, and their general relations to nearly allied substances are shown in the following formulæ:—

Cinnamic acid.....	$C_6H_5.CH : CH.COOH$
Amidocinnamic acid	$C_6H_4(NH_2).CH : CH.COOH$
Carbostyryl	$C_6H_4.NH.CH : CH.CO$
Quinoline.....	$C_6H_4.N : CH.CH : CH$
Leucolinic and quinolinic acids..	$C_6H_4(NH_2).CH_2.CO.COOH.$

An acid represented by the last formula should be readily hydrogenised, producing an *amidophenyl-lactic acid*,



isomeric with and closely related to tyrosine,

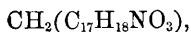


and differing from the latter only in having the amido-group attached to the phenylic instead of to the pyruvic residue: such isomeric tyrosines are produced by treating leucolinic and quinolinic acid with sodium-amalgam. Both products react with the mixed mercurous and mercuric nitrates, giving a red colour somewhat resembling the well-known tyrosine reaction, the difference between them and ordinary tyrosine being that, when fused with an alkali, they both yield aniline, whereas ordinary tyrosine similarly treated yields ammonia and para-hydroxybenzoic acid.

H. W.

Some Reactions of Morphine and its Congeners. By E. GRIMAUX (*Compt. rend.*, 93, 217—219).—Baeyer has shown that aromatic hydrocarbons and phenols unite with aldehydes in presence of sulphuric acid with elimination of water, and the liquids acquire various colours. As a source of formaldehyde, the author employed methylene acetochlorhydrin. When mixed with this substance and

sulphuric acid, morphine, codeine, and the morphine derivatives which the author has previously described, give an intense violet coloration. When the solution is allowed to stand several hours, diluted, and precipitated with ammonia, a new base is obtained. It is an amorphous yellow substance, very soluble in alcohol, slightly soluble in ether, insoluble in benzene. It probably has the composition—



and gives a violet coloration with sulphuric acid. Acetoxycodine gives a coloration when mixed with sulphuric acid alone, since it contains the elements of both morphine and formaldehyde. Thebaine and codallylene give an immediate red coloration with sulphuric acid, but do not give the same reaction as morphine and its derivatives. Thebaine is possibly a vinyl derivative of morphine. C. H. B.

Ethereal Derivatives of Morphine. By E. GRIMAUZ (*Compt. rend.*, **93**, 67—68).—The author has previously shown that the action of methyl and ethyl iodides on morphine gives ethers similar to those derived from phenol. Further experiments prove that this reaction is general. Iodopropane, allyl iodide, epichlorhydrin, and ethylene bromide act on morphine under the same conditions as ethyl iodide, giving new bases. In order to prepare the ethylene derivative, morphine is dissolved in alcoholic soda, an equal weight of ethylene bromide added, and the mixture heated until the reaction is only very slightly alkaline. The liquid is then evaporated to dryness, and the residue dissolved in boiling alcohol and allowed to crystallise. The compound thus obtained, *dicodethylene*, $(\text{C}_{17}\text{H}_{18}\text{NO}_3)_2 \cdot \text{C}_2\text{H}_4$, crystallises in small white needles insoluble in ether, but readily soluble in alcohol. When heated, it blackens, and above 200° decomposes without melting. Heated to 20° with sulphuric acid and ferric chloride, it gives a blue coloration. This reaction appears to be common to all the ethereal derivatives of morphine. *Dicodethylene hydrochloride* forms hard colourless prisms very soluble in water. If a solution of morphine in alcoholic soda is heated with methylene-acetochlorhydrin, the liquid evaporated to dryness, and the residue dissolved in hydrochloric acid, the addition of sodium carbonate causes the separation of acetoxycodine, $\text{C}_{17}\text{H}_{18}\text{NO}_3 \cdot \text{CH}_2 \cdot \text{AcO}$, in the form of a gummy mass, becoming hard when dried. It is decomposed when boiled with water, with formation of morphine, formaldehyde, and acetic acid, and dissolves in sulphuric acid in the cold, with production of an intense purple coloration similar to that of concentrated solutions of potassium permanganate. C. H. B.

Cinchamidine. By O. HESSE (*Ber.*, **14**, 1683—1685).—*Cinchamidine*, $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}$, a new alkaloid found in the aqueous mother-liquors from the purification of homocinchonidine sulphate, is obtained by the addition of ammonia to this liquid.

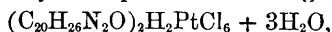
The precipitate is repeatedly recrystallised from hot alcohol, and purified by fractional precipitation with sodium tartrate from its solution in hydrochloric acid. The final precipitate, which consists of almost pure cinchamidine, is dissolved in sulphuric acid and treated

with a small quantity of potassium permanganate to remove all impurities.

It is then precipitated by ammonia, and recrystallised from alcohol, whereby it is obtained in colourless plates, needles, or thick prisms (m. p. 215°), which dissolve freely in chloroform. For a 2 per cent. alcoholic solution $[\alpha]_D = -98.4$. In acid solutions, its rotatory power is still higher. The base forms crystalline salts, the hydrochloride,



forms thick rhombic crystals, the neutral tartrate $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O})_2\text{C}_4\text{H}_6\text{O}_6 + 2\text{H}_2\text{O}$, colourless prisms sparingly soluble in cold water, and $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O} \cdot \text{H}_2\text{PtCl}_6$, anhydrous plates of an orange colour,



is amorphous.

Cinchamidine is frequently contained in commercial "cinchonidine purum."
W. C. W.

Homologue of Pelletierine. By A. ÉTARD (*Compt. rend.*, **92**, 460).—By slow distillation of a mixture of 50 grams ammonium chloride with 300 grams glycerol, 40 grams of a yellowish oil were obtained, boiling, after purification, at 155° . The analysis of this body leads to the formula $\text{C}_6\text{H}_9\text{NO}$ (hydroxypicoline), and its formation is represented by the equation $2\text{C}_3\text{H}_5\text{O}_3 + \text{NH}_4\text{Cl} = \text{HCl} + 5\text{H}_2\text{O} + \text{C}_6\text{H}_9\text{NO}$.

Hydroxypicoline is a colourless, refractive liquid (b. p. 155°) of strong odour and acrid taste, soluble in all proportions in water, alcohol, and ether. Its sp. gr. is 1.008 at 13° . Hydroxypicoline is a strong base, and reduces gold and silver salts. It forms precipitates with certain metals, with tannin, iodine, and bromine-water, mercuric chloride, auric chloride, and picric acid; the compounds with the last four are soluble in water and crystallisable.

The platinochloride, $\text{C}_6\text{H}_9\text{NOClH} \cdot \text{PtCl}_4$, crystallises from a concentrated solution in yellow needles. The mother-liquors from this salt are reduced when boiled, and give a greenish-yellow insoluble compound of the formula $(\text{C}_6\text{H}_7\text{N})_2\text{PtCl}_4$.

The aurochloride, $\text{C}_6\text{H}_9\text{NO} \cdot \text{AuCl}_3$, is crystallisable and melts at 154° .

When oxidised by dilute nitric acid, hydroxypicoline gives a small quantity of pyridine, together with carbonic anhydride and hydrocyanic acid. When fused with potassium hydroxide it is slowly decomposed with evolution of hydrogen. The constitutional formula of hydroxypicoline is probably $\text{C}_5\text{H}_4\text{N} \cdot \text{C}_2\text{H}_2\text{OH} \cdot \text{H}_2$. Its properties and composition show that it is homologous with the base *pelletierine*, extracted by Tanret from pomegranate-bark, and with the base $\text{C}_8\text{H}_{13}\text{NO}$, which Wurtz obtained by the distillation of ammonia-aldol. C. W. W.

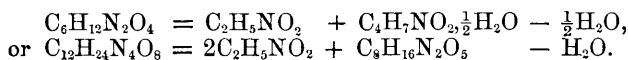
Biliary Acids in Toxicological Researches, and the Chemical Nature of Selmi's Ptomaines or Cadaveric Alkaloids. By A. CASALI (*Gazzetta*, 1881, 312—319).—This paper consists chiefly of theoretical speculations on the chemical constitution of the ptomaines, which the author regards, not as true alkaloids, but as *amidated compounds acid or basic*.
H. W.

Products of the Decomposition of Protein Compounds. By A. BLEUNARD (*Compt. rend.*, **92**, 458).—*Glucoprotein*, $C_6H_{12}N_2O_4$, is oxidised by bromine in presence of water, with production of gelatin-sugar, and an acid body having the formula $C_4H_7NO_3 + \frac{1}{2}H_2O$. The latter is an amorphous, yellowish mass, hard and brittle at ordinary temperatures, and becoming syrupy at 100° ; very soluble in water and in alcohol.

Boiled with water and moist cupric carbonate, it gives two compounds, $C_4H_7NO_3 \cdot CuO$ and $(C_4H_7NO_3)_2CuO$, the first of which is insoluble, the second soluble, in alcohol. It also forms compounds with the oxides of lead, zinc, mercury, and silver, but not with the oxides of the metals of the iron-family.

The leucine, $C_4H_7NO_2 + \frac{1}{2}H_2O$, obtained by Schützenberger from isinglass and by the author from deer's horn, absorbs bromine in the proportion indicated by the equation $(C_4H_7NO_2 + \frac{1}{2}H_2O) + H_2O + 2Br = 2BrH + C_4H_7NO_3 + \frac{1}{2}H_2O$. The acid body obtained by this reaction gives the same reaction with cupric carbonate as that just described (*supra*).

The constant presence of water in the leucine and its oxidation-product, would make it probable that the glucoprotein is formed by the union of a leucine and a leucine with elimination of water, *e.g.* :



The equivalents of the glucoproteins and the leucines might then be doubled, and the general formulæ, $C_mH_{2m}N_4O_8$ and $C_nH_{2n}N_2O_5$, adopted for them. C. W. W.

The Existence of Liebreich's Protagon in the Brain. By A. GAMGEE and E. BLANKENHORN (*Proc. Roy. Soc.*, **29**, 151–156).—**A Note on Protagon.** By A. GAMGEE (*ibid.*, **30**, 111).—Protagon is the name given by Liebreich to a crystallised substance, which he obtained in 1865, by treating brain, previously freed from blood, with ether and water, and digesting the undissolved residue in alcohol of 85 per cent. at a temperature of 45° . It crystallises from the alcoholic solution in needles having, according to Liebreich's analysis, the composition $C_{116}H_{241}NO_{22}P$. It is soluble in glacial acetic acid, and separates from the solution at low temperatures in crystals having the same composition.

The existence of protagon as a definite principle has, however, been called in question by Diaconow, Hoppe-Seyler, and Thudichum, who regard it as a mechanical mixture of lecithin, $C_{44}H_{90}NPO_8$, with a non-phosphorised body called *cerebrin*. These bodies, however, are both amorphous and highly hygroscopic, and it is rather remarkable that when simply mixed, they should produce a non-hygroscopic crystalline body like protagon.

With the view of throwing further light on this disputed question, the authors of the present paper have made careful analyses of protagon prepared by a modification of Liebreich's process. Perfectly fresh ox-brains, freed as completely as possible from blood and adhering membranes, were digested for 18–24 hours in a large incubator kept

constantly at 45°. The liquid was filtered whilst hot, and the insoluble matter was again treated with fresh quantities of spirit, this proceeding being repeated four or five times, as long indeed as the filtrate when cooled to 0° deposited a fair quantity of white flocculent precipitate. This precipitate was collected on a filter and then thoroughly and repeatedly shaken with ether in a stoppered bottle, in order to dissolve cholesterin and other bodies soluble in ether. The ether having been removed by decantation and filtration, the undissolved matter, after being pressed between filter-paper, was dried over sulphuric acid or phosphoric oxide; and the resulting snow-white mass was pulverised, moistened with a little water, and digested for many hours with alcohol at 45°. From the filtered liquid, if allowed to cool very gradually, the protagon separates in the form of microscopic crystals, mostly arranged in rosettes.

Seven analyses were made of protagon thus prepared, two from dog-brain once recrystallised, one from horse-brain four times crystallised, four from ox-brain twice recrystallised, and one from the same, three times recrystallised. These analyses all agreed very closely, and gave as a mean result—

C.	H.	N.	P.
66.39	10.69	2.39	1.068

leading to the formula, $C_{166}H_{308}N_5PO_{35}$, which requires 66.45 per cent. C, 10.66 H, 2.42 N, 1.07 P, and 19.40 O. These results are regarded by the authors as establishing beyond doubt the definite, and within certain limits, the stable character of protagon.

Thudichum on the other hand (*Annals of Chemical Medicine*, 1879, p. 254) regards protagon as an impure body, consisting of a mixture of many organic substances, and states in particular that he obtained from it a considerable quantity of potassium, amounting to 0.76 per cent.

In consequence of this statement, a specimen of protagon prepared as above described, and twice recrystallised from alcohol, was placed in the hands of Dr. Roscoe, who, on examining it spectroscopically, failed to detect any potash in the incinerated mass from 0.1 gram of substance. With the carbonised mass from 1 gram, he obtained the potassium-line (α) very faintly, and from comparative experiments with a dilute solution of a potassium salt, he estimates the quantity of potash in 1 gram of the substance as not exceeding $\frac{1}{20}$ mgrm., that is to say, 1 part in 20,000. The carbonised residue of 1 gram of protagon, when carefully oxidised with nitric acid, yielded on ignition a small quantity of fused metaphosphoric acid, weighing 0.0278 gram, and equivalent to 1.08 per cent. of phosphorus (Roscoe, *Proc. Roy. Soc.*, 30, 113).

Thudichum, on the other hand (*ibid.*, 278), attributes the faintness of the potassium spectrum just mentioned, to the presence of phosphoric acid in the protagon-residue, and points out that salts of the alkalis and earths which are more or less fixed at high temperatures, give either no spectra at all, or spectra which are very faint in comparison with those given by the volatile compounds of the same metals, such as the chlorides and bromides. In reply to these remarks, Roscoe

(*ibid.*, 32, 35) states that traces of potassium phosphate can easily be detected by the spectroscope, even in presence of a large excess of phosphoric acid, and he therefore maintains his first estimate of the proportion of potassium in the spectrum of protagon submitted to him by Dr. Gamgee. In another specimen twice recrystallised, he finds by gravimetric analysis 0.0236 per cent. potassium, that is to say, only one-thirtieth of the amount said by Dr. Thudichum to be present in protagon. He concludes his note with the following remark: "That the first crystallisations of a proximate principle of the brain, such as protagon, should contain a trace of potash salts, is what would naturally have been anticipated from a knowledge of the nature of the soluble salts of the brain; and therefore to argue against the individuality of protagon because of the presence of 0.0236 per cent. of potassium in a second crystallisation-product, appears to be entirely fallacious."

H. W.

Physiological Chemistry.

Animal Heat. By A. D'ARSONVAL (*Compt. rend.*, 93, 83—86).—During the incubation of the egg, there is an absorption of heat, although oxygen is absorbed and carbonic anhydride given off in large quantity. During sleep or complete rest, much oxygen is absorbed, but the development of heat is small; the proportion of carbonic anhydride given off varies slightly. In scarcely any case is there agreement between the amount of heat actually evolved and that calculated from the products of respiration, &c. The difference is due partly to the fact that animal combustions are of the nature of fermentation, as Claude Bernard pointed out, and partly to the fact that the animal body is the seat not only of oxidation, accompanied by a development of heat, but also of reduction and organic syntheses, accompanied by an absorption of heat. The chemical method takes into account the resultant of all the combustions, the calorimetric method gives the difference between the thermic effects of the oxidations, and that of the reductions and syntheses. C. H. B.

Nutritive Value of Gelatin. By OERUM and DITZEL (*Bied. Centr.*, 1881, 178—179).—A dog weighing 11 kilos. was the subject of experiment. After being deprived of food for three days, it was fed for nine days on 45 grams of gelatin and about 200 c.c. of water; the nitrogen was estimated in the urine by Liebig's method, and was during the fasting period 2.385 grams, during the time he was fed on the gelatin 7.105 grams daily; the nitrogen so voided in the urine exceeded that taken in the food by 0.785 gram, diminishing the waste by 1.600 grams per day. The quantity of food was then increased to 50 grams of gelatin and 225 c.c. water, representing 7.025 grams nitrogen. The quantity found in the urine was then 7.519 grams, or a daily loss of 0.494 gram, and a constant decrease of

weight in the animal was the result. This was soon followed by polyurea or abnormal increase in the quantity of urine, and afterwards by hæmaturia, so that it would appear that the amount of gelatin cannot be increased sufficiently to supply the waste. A second experiment was made with a medium sized dog, which was left unfed for three days, and during the following five days received a daily ration of a mixture of 91 grams of meat, 125 grams flour, 50 grams butter, and 5 grams of extract of meat, together with about 400 c.c. water. The waste of nitrogen was covered by that contained in the food. The meat was then replaced by gelatin, containing as nearly as possible the same amount of nitrogen. The amount voided in the urine during a period of five days of this treatment became sensibly greater, and exceeded the quantity taken in the food. The gelatin was then withdrawn, and nothing but flour, butter, and extract given. The nitrogen consumed was daily 0.412 gram, that voided 2.287 grams.

The authors conclude that gelatin is of very much less nutritive value than albumin. J. F.

Absorption of Food passing through the Human Body.

By M. RUBNER (*Bied. Centr.*, 1881, 394—399).—The experiments were conducted for several days on healthy subjects, and with staple kinds of food. Great differences were observed in the absorption of the latter,—rye-bread, potatoes, and green vegetables burdened the intestines considerably, and produced large quantities of fresh and dry excrement. On the other hand, white bread, fresh meat, and eggs were absorbed to a much larger extent. The fat of butter appeared to be better digested than bacon fat. Carbohydrates are easily assimilated when contained in white bread, rice, and macaroni, but with difficulty from potatoes, rye-bread, and swedes. Nitrogen is most easily absorbed from meat, eggs, and animal substances generally; with difficulty, however, from rye-bread and vegetables.

J. K. C.

Importance of Inorganic Salts in Feeding Animals.

By N. LUNIN (*Bied. Centr.*, 1881, 392—394).—According to Forster animals dieted with food from which all inorganic salts have been removed, rapidly die off. This, in Bunge's opinion, is due at least partially to the formation of free sulphuric acid from the albuminoid sulphur, and the consequent abstraction of basic constituents from the intestines. To throw light on this question, the author made some experiments on mice. Five mice fed with cane-sugar and casein from which the ash constituents had been abstracted, lived from 11 to 21 days. When enough sodium carbonate was added to neutralise possible sulphuric acid, six mice on the above diet lived from 23 to 36 days. With sodium chloride instead of carbonate the animals lived from 10 to 20 days only, and with the ash-constituents of milk added they lived only from 20 to 31 days. On milk alone, the mice existed for some months without showing signs of illness; but when dieted with albuminoids, cane-sugar, salt and water, they did not live longer than 20 to 30 days. From this the author concludes that milk must contain something else besides casein, fat, milk-sugar, and

salts, which is necessary to life, or else that milk-sugar cannot be replaced by cane-sugar.

J. K. C.

Effect of Maté on the Gases in the Blood. By A. D'ARSONVAL and COUTY (*Compt. rend.*, **93**, 86—88).—Infusion of *maté* in large or repeated doses injected into the veins or absorbed by the stomach, exerts a well marked effect on the amount and composition of the gases in both the venous and arterial blood of the dog. The total volume of gas is considerably diminished, sometimes by one-third or even one-half the normal amount. The proportion of carbonic anhydride diminishes more rapidly than that of the oxygen, so that the ratio of the latter to the former is higher after the administration of the *maté* than before.

C. H. B.

Estimation of the Amylolytic and Proteolytic Activity of Pancreatic Extracts. By W. ROBERTS (*Proc. Roy. Soc.*, **32**, 145—161).—The term *ferment* has hitherto been applied to two groups of agents, which, although nearly allied in origin and mode of action, nevertheless belong to essentially different categories. The *organised* or *formed ferments*, of which yeast is the type, are independent organisms with powers of growth and reproduction, and the transformations which constitute their special characteristics as ferments are inseparably associated with the nutritive operations of these organisms. The ferment power cannot be separated from the ferment organism by any method of filtration or by any solvent. The *soluble ferments*, on the other hand, pass freely into solution in water; their action is dissociated from the life of the gland-cells which produced them, and they are wholly devoid of the power of growth and reproduction. The author, following Kühne, designates these soluble ferments as “enzymes,” and further proposes to designate their action as *enzymosis*, and its nature as *enzymic*.

The pancreas is the source of two ferments or enzymes of capital importance in the digestion of food, viz., an amylolactic enzyme, called *pancreatic diastase*, and a proteolytic enzyme, called *trypsin*. The pancreas also takes an important share in the digestion of fats; but whether this power is due to an enzyme or to an agent of different character is a question not yet determined. The present paper concerns itself solely with the amylolytic and proteolytic functions of the pancreas.

Estimation of the Amylolytic Activity of Pancreas Extracts:—Dias-tasimetry.—The method adopted by the author for this purpose consists in ascertaining the quantity of starch-mucilage of known strength which can be transformed by a unit-measure of a diastasic solution to the point at which it ceases to give a colour-reaction with iodine, in a unit of time and at a fixed temperature. The vanishing point of the colour-reaction is called the *achromic point*.

The amount of amylolytic work which can be done, or in other words, the amount of standard starch-mucilage which can be brought to the achromic point in a given time by a given sample of pancreatic extract, is exactly proportional to the quantity of the extract employed, provided the products of the *enzymosis* do not accumulate in

the solution to such a degree as to interfere with the action, which will not be the case if the starch-mucilage used is sufficiently dilute. The mucilage used in the author's experiments was of the strength of 1 per cent. This law of proportionality may perhaps be regarded as applicable to the action of all enzymes, which indeed, having no power of growth or multiplication, conform in this respect to the law which governs the action of ordinary chemical agents.

The fundamental rule governing the relations of quantity and time in the action of an enzyme is that of *inverse proportion*, that is to say, a double quantity of an enzyme will do a given amount of work in half the time, &c. This rule, however, is apparently modified by another, namely, that *an enzyme liberates its energy at a progressively retarded rate*. In regard to the action of pancreatic extract upon starch-mucilage, the rule of inverse proportion between quantity and time was found to hold good within considerable limits, as shown by the following table, giving the results of experiments in which 10 c.c. standard starch-mucilage of the strength of 1 per cent. diluted with water up to 100 c.c., was subjected to the action of pancreatic extract at the temperature of 15°. The "calculated" time in the third column was obtained by taking the middle observation of each set as a standard of comparison.

Quantity of pancreatic extract employed.	Time in which the achromic point was reached.	
	Found.	Calculated.
I. { 0.02 cub. cent.	34 minutes	36 minutes
{ 0.04 "	18 "	18 "
{ 0.08 "	9 "	9 "
{ 0.10 "	7 "	7½ "
{ 0.20 "	3 "	3½ "
II { 0.4 "	4½ "	5 "
{ 0.2 "	10 "	10 "
{ 0.05 "	40 "	40 "

In both these sets of observations the inverse time-rate comes out with a very near approach to exactness. When, however, only a relatively small quantity of pancreatic extract was employed, the attainment of the achromic point was postponed beyond the term indicated by the rule. Thus when 0.004 c.c. of the extract was employed, the achromic point was reached in 125 minutes; consequently with 0.0005 c.c. extract the time should, according to the rule, have been 1,000 minutes, but it was actually 1,380.

Influence of Temperature.—The action was found to increase in energy (or speed) from 0° to 30°; thence to 45° it continued steady; above 45° it became less and less energetic, and finally ceased between 65° and 70°.

Comparative Diastasic Values of different Pancreatic Extracts.—The diastasic value of an extract is expressed, in the author's system, by

the number of cubic centimeters of standard mucilage, which can be brought to the achromic point by 1 c.c. of the extract to be tested in five minutes at a given temperature. By this mode of estimating, the author found that the extract obtained from the pancreatic tissue of the pig has at 40° a mean diastasic value of 100, those of the ox and sheep at the same temperature having the values 11 and 10 respectively. Filtered human saliva has a diastasic value of 10 to 17 at 40°, and its energy varies with the temperature in exactly the same manner as that of pancreatic extract (p. 1052). *Malt diastase* has a diastasic value of 4 to 5 at 40°, increasing to 10 at about 60°, above which it diminishes, but does not cease entirely until the temperature is raised to 80°. Several specimens of human urine showed a diastasic value of 0.03 to 0.13 at 40°.

Proteolytic Activity of Pancreatic Extracts.—Trypsimetry.—Milk digested with pancreatic acid acquires the property of curdling when boiled. The onset of this reaction occurs earlier or later according to the activity of the extract, and the quantity of it employed; and the time of its advent may be fixed with sufficient accuracy to serve as the basis of a method of measuring the proteolytic activity of pancreatic extracts. The reaction in question depends on the production, as a first step in the digestion of casein, of a modified form of that body—termed by the author “metacasein”—which resembles casein in being curdled by acetic acid in the cold, but differs from it in being curdled also by simple boiling. These two reactions together distinguish metacasein from all other proteids. The property of curdling when boiled, which may be called the *metacasein reaction*, continues observable in milk undergoing tryptic digestion until near the end of the process; it then disappears somewhat abruptly, the milk remaining fluid when boiled. We may therefore speak of the *onset-point* and the *vanishing-point* of the metacasein reaction, these two points marking respectively the initial and terminal limits of the principal phases in the digestion of milk by pancreatic extract. Before, however, the onset-point of the reaction, *i.e.*, distinct curdling, is attained, its approach is indicated by an appearance of soiling of the sides of the test-tube in which the milk has been boiled. This appearance is due to incipient coagulation, which presently develops into pronounced curdling.

When milk is diluted with water, the occurrence of the metacasein reaction is postponed, the time of postponement varying with the degree of dilution.

The method of trypsimetry adopted by the author consists in ascertaining how many cubic centimeters of milk can be brought to the onset of the metacasein reaction in five minutes by 1 c.c. of the extract to be tested at a given temperature, attention being paid, as in the case of diastase, to the relations of tryptic action to quantity, time, and temperature.

The rule of inverse relation between quantity and time, which was found to be valid within a wide range in the case of diastase and starch, holds good in the case of trypsin and milk within narrow limits only. When the time of action exceeds eight or ten minutes the advent of the metacasein reaction is postponed beyond the term

indicated by the rule of inverse proportion, and this postponement increases as the time of action is lengthened. When the vanishing-point of the metacasein reaction is taken as the point of comparison, the results approximate more nearly to the rule of inverse proportion, especially at low temperatures; nevertheless the evidence points in the same direction, indicating that trypsin, like diastase, exhausts itself in action at a progressively retarded rate. When the onset-point of the reaction falls between three and six minutes, the inverse time-rate gives a trustworthy basis of calculation, but not beyond these limits.

Tryptic enzymosis is exceedingly sensitive to temperature. The action of trypsin on milk increases in energy from 0° to 60°, but above this point there is a rapid fall, the action being finally arrested between 75° and 80°. There is not, as with diastase, any range or platform of indifferent temperature.

The following table shows the enzymic values of twelve samples of pancreatic extract prepared with single glands from four pigs, four oxen, and four sheep, killed for the market. All the observations were made at 40°. D stands for diastasic, T for tryptic value:—

Pig.	Ox.	Sheep.
No. 1 { D = 166 { T = 64	No. 5 { D = 8 { T = 64	No. 9.... { D = 5 { T = 125
No. 2 { D = 100 { T = 83	No. 6 { D = 10 { T = 50	No. 10.... { D = 12 { T = 83
No. 3 { D = 100 { T = 72	No. 7 { D = 9 { T = 42	No. 11.... { D = 14 { T = 64
No. 4 { D = 100 { T = 64	No. 8 { D = 13 { T = 83	No. 12.... { D = 4 { T = 28

The oscillations in the two enzymic values do not exhibit any regular relation to each other.

The most appropriate standard of temperature for the valuation of tryptic activity is 40°, as it corresponds very nearly with the temperature at which trypsin operates in the normal digestion of warm-blooded animals; but it is more convenient to perform the testing at or near the ordinary temperature of the room, say at 20°; and the author has ascertained that the values of T obtained at this temperature may be converted with sufficient accuracy into the corresponding values at 40° by multiplying them by 3·5.

H. W.

Relation of Wool to Body Weight in Merino Sheep. By F. MITSCHKE-COLLANDE (*Bied. Centr.*, 1881, 399—403).—According to some sheep breeders, the larger sorts of merino are to be preferred, because of their yielding a better return both in flesh and wool for the fodder allowed. The author, however, after 25 years' experience, finds the opposite to be the case, as the build of the sheep has more to do with their fattening properties than the absolute size, and larger quantities of wool are obtained from small sheep in relation to a given weight than in the larger kinds, the relative increase amounting to from 20 to 30 per cent.

J. K. C.

Blue Milk. By F. NEELSON (*Bied. Centr.*, 1881, 418—422).—The blue appearance which milk sometimes presents after standing a few days is due to an organism which is allied to bacteria, and can be transplanted into other samples of milk and various solutions. It thrives according to the proportion of acid present and the condition of the casein; it appears after a certain degree of acidification has taken place, and prevents the further formation of acid. The casein must also be unchanged: it is then held in solution during the blueing process. The blueing occurs only in presence of oxygen, and is attended with evolution of carbonic anhydride. J. K. C.

Relation of the Urea to the Total Nitrogen of the Urine in Disease. By W. J. RUSSELL and S. WEST (*Proc. Roy. Soc.*, 30, 439—444).—Professor Parkes has shown that in health 90 per cent. of the nitrogen in urine is eliminated in the form of urea; and the object of the experiments recorded in the present paper is to ascertain whether this proportion holds good also in disease, or whether, under altered conditions, some of the nitrogen may not be excreted in another form.

The nitrogen in the urea was determined by decomposing that compound with sodium hypobromite and measuring the volume of the nitrogen evolved, as already described by the authors in this Journal (1874, p. 749). The total nitrogen was determined by burning the evaporation-residue with copper oxide, and measuring the volume of the nitrogen evolved.

The result of a large number of observations on various cases of disease was to prove that the chemistry of the urine remains essentially the same in disease as in health; and that the generalisation of Professor Parkes is true in either case—so that the nitrogen of the urea may in all cases, except one to be mentioned below—be regarded as a measure of the total nitrogen, and as forming 90 per cent. of it.

The following table shows the percentage of urea-nitrogen in the different groups of cases examined:—

Pneumonia (6 cases)	90·0
Jaundice (Case 1)	85·7
„ (Case 2)	90·2
Albuminuria (2 cases)	86·0
Collected cases.....	93·8
Dieted cases.....	90·1
	<hr/>
Mean of all	89·3
	<hr/>
Mean, excluding the jaundice and albuminuria cases.....	91·3

The exception above alluded to is found in the rare cases of acute yellow atrophy of the liver; but even in these cases it is doubtful whether the observed replacement of the urea by leucine and tyrosine is a constant phenomenon. In a case of acute fatty atrophy of the liver the urea was still normally formed, leucine and tyrosine being absent.

H. W.

Amount of Nitrogen Excreted in the Urine by Man at Rest. By S. WEST and W. J. RUSSELL (*Proc. Roy. Soc.*, **30**, 444—449).—The experiments were made upon three men kept at absolute rest, and upon a diet reduced to the lowest limit compatible with health.* Under these circumstances the amounts of nitrogen ingested in the food and obtained from the urine were as follows:—

	I.	II.	III.
Nitrogen ingested	7·0	7·0	5·6
Nitrogen in urine	8·6	8·64	6·4

In all three instances the amount in the urine is in slight excess of that in the food, so that all the nitrogen here obtained may be regarded as representing tissue-waste, since there was no surplus in the food to increase the amount in the urine.

The mean of the three results is $\frac{23\cdot64}{3} = 7\cdot87$, or approximately 8 grams, which may be regarded as the minimum amount of nitrogen excreted per diem by a healthy man. This is equivalent to 17 grams or 260 grains of urea. This result agrees very nearly with those obtained by other observers in the cases of individuals in a state of starvation, or kept on insufficient diet, or on non-nitrogenous food.

H. W.

Researches on the Colouring Matters of Human Urine, with an Account of their Artificial Production from Bilirubin and from Hæmatin. By C. A. MACMUNN (*Proc. Roy. Soc.*, **30**, 250—252, **31**, 26—36 and 206—236).—Urobilin is a pigment discovered in human urine by means of the spectroscope, but not hitherto isolated. Before its discovery, Jaffé, by acting on human bile with nitric acid, and on dog's bile with hydrochloric acid, and subsequent treatment, had obtained a pigment which gave the same spectrum and behaved in the same manner to reagents as urine containing urobilin. The author of the present paper has detected a pigment exhibiting very similar characters in the bile of seventeen animals, but most abundantly in that of the mouse. He has also shown that human urine always gives an absorption-band at F, which is usually affected by reagents in the same manner as choletelin, the pigment obtained from bile by Jaffé; and that if this band is not so affected, another pigment called *uroolutein* is present.

The isolation of urobilin was effected as follows: Some urine, which by preliminary spectroscopic and chemical tests showed a large amount of urobilin, was precipitated with neutral and basic lead acetate respectively and filtered; the filtrate, if it gave an absorption spectrum, was reprecipitated until the band disappeared; the united precipitates were exhausted with alcohol acidulated either with sulphuric or with hydrochloric acid; and the liquid was filtered. The filtrate, which had a fine red colour and gave the dark band F, was put in small quantities at a time, into a tap-funnel, a large quantity of water

* The subjects of these experiments were hospital-patients suffering from aneurism—a disease which produces mechanical rather than constitutional symptoms, so that, as far as this inquiry is concerned, they may be regarded as healthy men.

being added and then pure chloroform, and the red chloroform layer was separated off and filtered; on subsequent examination it was found in every instance to give the original spectrum. The chloroform was next evaporated off, and the residue repeatedly dissolved in chloroform, whereby a solution was finally obtained which gave on evaporation a brown-red shiny, amorphous residue, perfectly soluble in alcohol, chloroform, nitric, hydrochloric, acetic, and lactic acids, and in acidulated water, partially soluble in ether, benzene, and pure water, but quite insoluble in carbon bisulphide. The pigment is obtained in combination with sulphuric or hydrochloric acid, accordingly as one or the other acid is used in its preparation. The spectra of its various solutions—figures of which are given in the papers above quoted—show that they all contain the same pigment, which cannot be resolved into simpler components by the action of any solvents or reagents.

The spectroscopic characters of the pigment differ, however, accordingly as it is obtained from normal or from febrile urine, the latter giving a sharp black band at F, whereas the corresponding band of normal urine is less marked at the edges, and is less shaded than that of febrile urine. The band is well seen in the alcoholic solution of normal urine, and disappears when the liquid is treated with caustic potash, soda, or ammonia.

The results of the author's observations on urobilin and on the colouring matters of bile are summarised as follows:—1. Normal urine contains a body, as such, which is apparently identical with choletelin, and not with the body produced by the action of hydrogen peroxide on acid hæmatin.—2. Normal urine contains the chromogen of febrile urobilin, which can be prepared artificially by reduction of choletelin, and of the body produced by oxidation of hæmatoïn.—3. Human, ox, sheep, and pig bile contain a kind of urobilin, which differs in some respects from that excreted in urine; they also contain hæmatin.—4. It is highly probable that all the constituents of bile colouring matter are produced from hæmatin by reduction.—5. The hæmatin present in bile is probably due to the action of the bile-acids on hæmoglobin.—6. All the colouring matters of bile, including hæmatin, urobilin of biliary origin, bilirubin, &c., are oxidised to choletelin, and there is evidence to show that blood-serum contains this body, on its way to be excreted by the kidneys.—7. The absorption-bands seen in the bile of various animals are due to the presence of hæmatin and urobilin of biliary origin.—8. A pigment excreted in the urine in certain pathological conditions is derived from hæmatin by reduction, as it can be obtained by reducing acid hæmatin with zinc and sulphuric acid, or with sodium-amalgam. This pigment is not febrile urobilin, and as it is derived directly from hæmatin, it is best named *urohæmatin*.—9. The urobilin of bile is produced in the intestine.—10. The urobilin of bile may, in certain states of the system, appear in the urine, but under normal conditions it is oxidised into choletelin in common with the other bile-pigments, and comes to the kidneys as choletelin, while a part may pass into the urine as such; but a part becomes reduced in the kidneys to the chromogen of febrile, and perhaps also to the chromogen of normal urobilin, the former being

converted by strong oxidising agents into febrile urobilin, the latter by weaker oxidising agents into normal urobilin.—11. Many of the colouring matters of urine have been produced by the action exerted on these chromogens by the reagents designed to separate them.—12. While most of the urinary pigments may be traced back to the bile-pigments, there is evidence to show that some of them are derived from hæmatin directly, and that pigments derived from that source may entirely replace the normal pigments. H. W.

Nitrogenous Constituents of Excrement. By G. KENNEPOHL (*Bied. Centr.*, 1881, 389—391).—When the proportion of carbon to nitrogen in the food is increased beyond a certain point by the addition of light digestible non-nitrogenous fodder, the quantity of nitrogen in the fæces becomes greater. This, according to Killner, is due to the increased secretion of bile-constituents (gallic acid, colouring matters, and taurin), and of mucin, the amount of which in the fæces he holds to be a measure of the food digested. Kennepohl on repeating Killner's experiments, is unable to find any relation between the quantity of bile-constituents in the excrement and the amount of digested food, and thinks that the increased quantity of nitrogen is due to the depressive action on the digestion of protein exercised by the additional light non-nitrogenous fodders. J. K. C.

A New Line of Research bearing on the Physiology of Sugar in the Animal System. By E. W. PAVY (*Proc. Roy. Soc.*, 32, 418—432).

Action of Ammonia and its Salts, and of Hydrocyanic Acid on Muscle and Nerve. By T. L. BRUNTON and T. CASH (*Proc. Roy. Soc.*, 32, 384).

Physiological Action of β -Lutidine. By C. G. WILLIAMS (*Proc. Roy. Soc.*, 32, 162—170).

Chemistry of Vegetable Physiology and Agriculture.

Nutrition of the Lower Fungi. By C. v. NÄGELI (*Bied. Centr.*, 1881, 430—431).—The sources of nitrogen are amides and amines, ammonia salts, and nitrates (except for yeast-plant): nearly all carbon compounds which do not react too strongly acid or alkaline, or are not poisonous, may be employed as sources of carbon.

J. K. C.

Influence of Rochelle Salt on the Activity of Yeast. By M. HAYDUCK (*Bied. Centr.*, 1881, 491—493).—By permitting a 50 per cent. sugar solution to ferment, it was found that if Rochelle salt were present, the action of yeast was less violent, but was more complete and continued for a longer time. Rochelle salt also delays the growth of yeast, but does not affect the quantity. The activity of yeast

decreases as the strength of the sugar solution increases, but even when the solution is concentrated the yeast will still work. E. W. P.

Diastase of Kôji. By R. W. ATKINSON (*Proc. Roy. Soc.*, 32, 299—332).—This paper contains the results of an investigation into the nature of the material used in Japan for converting starch into sugar in brewing operations. This substance, “kôji,” is prepared from steamed rice, by allowing the spores of a fungus, mixed with the grain, to vegetate over the surface. The change is attended with great evolution of heat, and the rice suffers a loss of 11 per cent. calculated on the substance dried at 100°.

A solution of the soluble portion of the kôji thus prepared possesses properties analogous to those of malt-extract, although differing from the latter in some important respects. It rapidly inverts cane-sugar, and hydrates maltose and dextrin. It liquefies starch-paste, forming at first maltose and dextrin, but giving as ultimate products dextrose and dextrin. The principal change produced in the rice-grain by the growing fungus is to render the insoluble albuminoids previously existing in the rice soluble.

The chief use of kôji is in the production of *Saké*, the alcoholic liquid which is everywhere consumed in Japan. This liquid is prepared from steamed rice by digestion with kôji, the diastase of which converts the starch into fermentable matter. Kôji is also employed in bread-making and in the preparation of the well-known sauce “Soy,” which is likewise a product of fermentation, although its preparation is much more complicated, and has not yet been explained.

H. W.

Fermentation of Urea. By C. RICHET (*Compt. rend.*, 92, 730).—Ammoniacal fermentation of urea is set up by contact with the stomachs of men, dogs, or rabbits. It is probably due to an organised ferment, *torula*, described by Pasteur and Van Tieghem.

In a strong solution of urea (100 grams per litre), a portion of stomach or other organic tissue sets up a fermentation, but in a weak solution, or if the tissue is crushed, bacteria of putrefaction are developed, and only traces of ammonia are formed. The ferment develops well only in presence of albuminous matter.

C. W. W.

Studies on Evaporation. By P. SORAUER (*Bied. Centr.*, 1881, 190—195).—The author concludes, from an extended course of experiments, that evaporation is a physiological rather than a mechanical operation, and that the greater the superficial extent of leaf surface engaged in the formation of solid substance in the plant, the smaller is the percentage of evaporation. The temperature does not appear to influence the transpiration of moisture in plants, but light, according to the author and other observers, is a very important factor. Plants of the same species and under the same conditions, lose by evaporation in exact proportion to the new substance added to them. Plants grown in dry soils lose less in proportion to their total weight than those grown in moist earth. Several experiments were made to determine the effect of dry and damp air on growth. The general

results tend to show that moist air encourages the increase of the roots, stems, and leaf stalks, but diminishes the number of leaves. The effect of concentrated manures is to diminish the production of dry substance and of leaves, and in consequence a diminution of evaporation. The removal of leaves also diminishes the total amount of evaporation, and plants transpire more in the absence of carbonic anhydride than when an abnormal quantity is introduced into the atmosphere in which the plant is grown. J. F.

Researches on the Amount of Water appropriated by Agricultural Plants. By E. WOLLNY (*Bied. Centr.*, 1881, 467—469).—Many writers have attempted to prove that the amount of water transpired by plants is in excess of the quantity received by the soil. Experiments have been instituted to test the correctness or incorrectness of this statement. In the greater number of cases the amount of rain which falls is amply sufficient to replace the water which is evaporated from a surface of soil covered with vegetation; but in those cases in which the evaporation exceeds the rainfall, the amount of moisture in the soil previous to the commencement of vegetation suffices to make good the deficit. The water lost by evaporation and that gained by precipitation almost balance one another. Researches also show that the evaporation is greater the closer the plants grow to one another; hence on those soils which are not retentive of moisture the plants will suffer from drought if they be planted unusually close together. Manures also, by increasing the growth of plants, induce a greater amount of transpiration. To a certain extent the activity of plant growth is greater when the seed is sown early in the season, and therefore the evaporated water must be greater in quantity than if the crop be sown late, premising of course that the early sown crop is healthy. E. W. P.

Influence of Light on the Liberation of Carbonic Anhydride by Plants. By A. FAMINTZIN (*Bied. Centr.*, 1881, 211).—The results of the author's investigations are summarised thus. For a number of plants there is a maximum point of intensity; and when this is passed, the increased light has no further effect on the liberation of carbonic anhydride, but, on the contrary, causes liberation of a small amount of oxygen. A gas flame of 50 candle value is sufficient (if the dark heat rays are intercepted) to cause a vigorous disengagement of carbonic anhydride, but still decomposes but about one-third less than the available sum. The existence of a maximum point of intensity as regards the disengagement of oxygen is doubtless intimately connected with the phenomena of chlorophyll formation and transmutation. The proof of the existence of these maximum points of intensity should be of great value in researches on the growth of plants. J. F.

Influence of an Increased Quantity of Carbonic Anhydride on the Growth of Plants. By A. MAYER (*Bied. Centr.*, 1881, 211—212).—The author adversely criticises experiments of H. Detries on the growth of beets in an atmosphere of carbonic anhydride. He admits that in such an experiment an abnormal growth of leaf may

take place, but at the expense of other qualities of the plant, and believes that contrary effects are produced when experiments are made under conditions resembling those of nature or in the open field.

J. F.

Formation of Starch Grains. By A. F. W. SCHIMPER (*Bied. Centr.*, 1881, 195—197).—According to Nageli and Sachs, the shape and size of the starch grains in a plant depend to a large extent on their situation in the chlorophyll cells. If the latter are of a well-rounded form, the starch grains are disengaged freely, and attain regular forms and normal size, whilst if the former are from their position flattened or misshapen, the latter have not the same freedom of development, and are smaller.

The examination of a freshly-cut section of a plant not containing chlorophyll but forming starch, shows the starch grains surrounded, not by the ordinary plasma, but by spherical and spindle-shaped refractive particles, at whose expense the starch grains grow. They are called starch-formers by the author. They bear the greatest resemblance to chlorophyll, and are readily transformed into it by the action of light: further investigation of the subject leads to the conclusion that the two substances are identical, but in different stages of growth.

J. F.

Growth of Starch Grains. By A. F. W. SCHIMPER (*Bied. Centr.*, 1881, 479—482).—The author from his observations considers that starch grains are to be considered as consisting of radial crystalline aggregates (sphaerocrystals), differing, however, from ordinary sphaerocrystals by their power of swelling up, and should therefore be called crystalloids. The starch crystalloid does not occur alone, but in aggregates. All the properties possessed by starch, such as cleavage, &c., can be explained on this hypothesis.

E. W. P.

Influence of Light on the Germination of Seeds. By STEBLER (*Bied. Centr.*, 1881, 460).—Experiments in sun- and gas-light show that light assists the germination of certain seeds, such as grass seeds, and that these seeds will not germinate in the dark.

E. W. P.

Composition of Various Parts of Grapes. By E. MACH and K. PORTELE (*Bied. Centr.*, 1881, 414—416, comp. this vol., p. 126).—Must was separated into three kinds, namely, that which trickled free from the grape, that contained in the fleshy part of the fruit, and the juice pressed from the skins. After analysing the must at various stages of ripeness of the grape, the authors find that in the earlier periods more sugar is found in the core than in the skins, the reverse happening afterwards, when the greatest quantity of sugar is found in the free running juice. At first this sugar consists chiefly of dextrose, but in ripe fruit levulose predominates. The largest quantity of cream of tartar is found in the fleshy core of ripe fruit.

J. K. C.

Occurrence of Allantoin in Vegetable Organisms. By E. SCHULZE and J. BARBIERI (*Ber.*, 14, 1602—1605).—To detect the pre-

sence of allantoin in the *Platanus orientalis*, the young leaves, buds, or stems are dried and exhausted with hot water; the extract is mixed with lead acetate; and the filtrate, freed from lead by means of sulphuretted hydrogen, is concentrated by evaporation. After some time it deposits crystals of asparagine and allantoin. The asparagine can be removed by crystallisation or by precipitation as the copper salt.

W. C. W.

Chemical Composition of Aleurone-Grains. By S. H. VINES (*Proc. Roy. Soc.*, **30**, 387—393, and **31**, 59—63).—In a former paper (this Journal, 1880, Abstr., 482) the author gave the results of an investigation of the aleurone-grains of the blue lupin. The following is an abstract of the results obtained by an examination of the grains of some other seeds.

The aleurone-grains of the peony (*Pæonia officinalis*) consist of one proteid soluble in water (*hemialbumose*), and another insoluble in distilled water, but soluble in 10 per cent. NaCl solution and precipitable therefrom by boiling or by separation; in these respects, it corresponds with the *vegetable myosin* found in the seeds of the blue lupin. The peony grains do not appear to contain any substance (or at most a very small quantity of it) analogous to the vegetable vitellin which occurs in lupin grains, and is soluble in saturated NaCl solution.

The ground-substance of the aleurone-grains of the castor-oil plant (*Ricinus communis*) consists of hemialbumose and two globulins, one of which is soluble and the other insoluble in a saturated solution of NaCl or MgSO₄. The crystalloid consists of a globulin which is soluble in 10 and 20 per cent. NaCl solutions; after treatment with alcohol it becomes soluble in saturated NaCl and MgSO₄ solutions.

The aleurone-grains of the blue lupin dissolve readily in both these saturated solutions, and their solubility is not affected by treatment with alcohol. The solution, in quantity, gives a precipitate on boiling and on dilution.

The three kinds of aleurone-grains above mentioned represent three degrees of complexity of composition. In the peony, the whole grain dissolves readily in water; in the lupin it dissolves only partially in water, the residue being soluble in 10 per cent. NaCl solution; in *Ricinus* there is a morphological as well as a chemical differentiation; the ground-substance dissolves partly in water and partly in 10 per cent. NaCl solution, and in this respect it resembles the entire grain of the lupin, whereas the crystalloid dissolves very slowly in a 10 per cent. NaCl solution.

Alcohol does not render the vegetable globulins insoluble in solutions of neutral salts; in fact all the above-mentioned reactions are exhibited by aleurone-grains which have lain in alcohol for a considerable time; and the same is true of the globulins after their extraction from the aleurone-grains.

The crystalloids of *Ricinus*, which in their natural state are quite insoluble in saturated NaCl or MgSO₄ solutions, are rendered easily soluble therein by treatment with alcohol; if, however, they are

subsequently washed with water, they lose their solubility in these saturated salt-solutions and regain it only after renewed treatment with alcohol. The change thus produced by alcohol appears to consist in the conversion of a myosin substance into a vitellin substance, and this conversion seems to be closely connected with the removal of water from the former.

The investigation of the crystalloids of a variety of plants with the reagents above mentioned has led to the following results:—A. Crystalloids insoluble in NaCl or $MgSO_4$ solution: *Musa Hillii*, *M. Ensete*.—B. Partly soluble in the same: *Sparganium ramosum*.—C. Crystalloids entirely soluble: *a.* Readily soluble in both 10 per cent. saturated solutions: *Bertholletia*; pumpkin; artificial crystals.—*b.* Slowly soluble in 10 per cent., more readily in 20 per cent. solutions; soluble in saturated solutions after treatment with alcohol: *Ricinus communis*, *Viola elatior*, *Linum usitatissimum*.

No definite relation appears to exist between the crystalline form of the crystalloids and their solubility in solutions of neutral salts. According to Schimper (*Unters. über die Proteinkrystalloide*, 1879) all the crystalloids above mentioned belong either to the regular or to the hexagonal system.

The aleurone-grains of the sunflower (*Helianthus annuus*) contain: (1) A substance (vegetable peptone or hemialbumose), which is soluble in water. (2) A substance which is soluble in 10 per cent. NaCl solution, and precipitable therefrom by saturation with NaCl, and therefore belongs to the group of myosin-globulins. (3) A substance which is soluble in saturated NaCl solution, whether the grains have been treated with alcohol or with ether, and therefore belongs to the group of vitellin-globulins; and (4) A substance which, like the crystalloids of *Ricinus* above described, is soluble in saturated NaCl solution only after treatment with alcohol.

The aleurone-grains of the Brazil-nut (*Bertholletia excelsa*) consist of vegetable peptone and of globulins, the one belonging to the myosin, the other to the vitellin group. Weil (*Zeitschr. physiol. Chem.*, Bd. 1, 1877) has shown that the crystalloids of these grains consist of pure vitellin: hence the peptone and the myosin must be contained in the ground-substance of the grains.

The proteid-substances detected in aleurone-grains may be classified as follows:—

I. *Soluble in distilled water*:—

Vegetable peptone (hemialbumose).

II. *Insoluble in distilled water*:—

a. Soluble in 10 per cent. NaCl solution: Globulins.

(α .) *Insoluble in saturated NaCl solution*:

Vegetable myosin.

(β .) *Soluble in saturated NaCl solution after treatment with alcohol*:

Substance of crystalloid of *Ricinus*, &c.

(γ .) *Soluble in saturated NaCl solution after ether or alcohol*:

Vegetable vitellin.

b. Insoluble in 10 per cent. NaCl solution : Albuminates.

(α .) Soluble in 1 per cent. Na_2CO_3 solution.

(β .) Soluble in dilute KHO.

The peculiar proteid which constitutes the crystalloid of *Ricinus*, and occurs in the grains of *Helianthus*, is placed alone by the author ; for although before treatment with alcohol it resembles myosin in its properties, and vitellin after that treatment, it differs from both these substances in being less readily soluble in 10 per cent. NaCl solution.

The paper concludes with a classification of the aleurone-grains of different plants, founded chiefly on their microchemical characters.

H. W.

Injurious Effect of Furnace Gases on the Forests of the Upper Harz. By REUSS (*Dingl. polyt. J.*, **241**, 124—132, and 204—212).—The author discusses very minutely the injuries received by the trees in the Upper Harz from the gases escaping from various smelting furnaces. Having pursued this subject in conjunction with Schröder for several years, he finds that since 1867 the injurious effects on vegetation caused by furnace gases have been more than doubled. These gases, apart from being detrimental to men, cattle, soil and pasture, ruin forests and assist in rendering soil unfit for cultivation, by destroying the surface, and causing the particles of soil to be disintegrated.

To obviate these injurious effects, it is in the first place necessary to ascertain which of the constituents of furnace gases are the active ones. Furnace gases consist chiefly of sulphurous acid and oxides of lead and zinc. The changes which deciduous trees and fir trees undergo when subjected to the action of sulphurous acid are well known : it is difficult, however, to ascertain whether the damage is done by furnace gases, since injurious effects are also produced by insects, fungi, frost, dust, or poor soil, the appearance of which greatly resembles those exhibited by furnace gases, and the difference can be distinguished only after considerable experience. In many cases it is impossible to find any difference, *e.g.*, when the changes are the result of the influence of dust or poor soil on vegetation. In order to prove that visible injuries originate from the influence of furnace gases, the cones of fir trees were tested for sulphuric acid ; although in most cases satisfactory results were obtained, it is thought that chemical analysis alone is insufficient and cannot be considered as conclusive without comparison with the microscopical examination. The author has examined a large number of fir trees, and found that as the percentage of sulphuric acid in the cones increases so much more does the plant suffer. Fir trees were completely destroyed with 0.323 and 1.332 per cent. of sulphuric acid in the cones.

With regard to the resistance which plants offer to furnace gases, experiments were made which proved that fir trees are the most sensitive. The following is the order of resistance:—1. Oak ; 2. Norway maple, field maple ; 3. ash, large leaved maple ; 4. alder, aspen ; 5. hawthorn, apple-tree ; 6. linden ; 7. hornbeam, mountain ash, birch ; 8. hazel ; 9. elm, chestnut ; 10. beech ; 11. larch ; 12. fir ; 13. pine ; 14. white pine (deal).

D. B.

New English Kinds of Wheat. By F. HEINE (*Bied. Centr.*, 1881, 403—405).—As suitable for cultivation in Germany the author mentions Spalding's prolific, Sheriff's square-head, and Rivett's bearded; the latter may be sown between September and January.

J. K. C.

Djugara, a New Kind of Corn. (*Bied. Centr.*, 1881, 424—425).—The ground seeds of this plant make a meal-like flour; it is extensively grown in Central Asia, where 100 kilos. seed are required for one hectare. The crop averages 2,800 kilos. seed per hectare, and a large quantity of straw, which is greedily devoured by cattle. The plant ripens in three months. Analysis of the seeds gave the following numbers:—Water, 11·6; fat, 2·8; starch, 53·5; dextrin and sugar, 10·8; fibrin, 9·4; protein, 10·1; and ash, 1·9 per cent.

J. K. C.

Feeding Value of Alpine Hay. By E. KRAMER (*Bied. Centr.*, 1881, 456—460).—Alpine hay has long been noted for its superiority over the hay made in the vale.

Botanical examination shows that some samples contain many juicy and evergreen plants, in some cases the *Glumaceæ* are represented only by *Carex sempervirens*, and the *Papilionaceæ* by *Anthyllis alpestris*; *Meum mutellina*, which contains ethereal oils, is present in large quantities. In other hays there are 16 species of *Glumaceæ* present.

The chemical analysis shows that Alpine hay is much richer in albuminoids, fat, and nitrogen-free extract than meadow hay, which contains more fibre. The reasons for this difference are that the period of vegetation is so much shorter than down in the valleys; at 4,000 feet the period extends over 200 days, at 6,000 feet to 132, and at 8,000 feet to 92 days, hence there is not sufficient time for the hard fibre to be formed.

With increase of height, the internodes of the stems are shortened, which produces a relative increase in the number of leaves; also a larger number of the evergreen plants (*Carex sempervirens*, *Daphne striata*, &c.) are found in the meadow hay, so that the proteids are produced and stored up during the winter.

E. W. P.

Experiments with Darnel and Lucerne as a Mixture for Meadows. By WITTMANN (*Bied. Centr.*, 1881, 212).—A mixture of the seeds of this plant in the proportion of 24—26 kilos. with 6—8 of lucerne, or 70 to 80 kilos. of esparsette is recommended for pasture, on poor clay and sandy soils. The ground should be deeply tilled in autumn and well manured, the seed sown in early spring, each kind separately, and barley sown as a shelter; the author says it will last 15 to 20 years, and yield rich fodder.

J. F.

The Sand Vetch: a New Fodder Plant. By KUHN (*Bied. Centr.*, 10, 209—210).—This plant was introduced accidentally amongst other seeds, into the district of Magdeburg, but is known to exist in other parts of Germany, and is said by some persons to be identical with the large Russian vetch grown in the north of Scotland; but to the author this identity is not proved. It thrives exceedingly in sand, and Jordan who has cultivated it says that it yields a crop double that

of lupines; the hay and chaff are admirable fodder for sheep, and the seed is greedily eaten by cattle and pigs, their weight increasing rapidly under such feeding.

He considers it of such value that experiments should be freely undertaken to verify his statements. The seeds appear in the catalogues of some seedsmen only, and in the class of ornamental plants under its botanical name, *Vicia villosa*, Roth. J. F.

Analysis of Plantain Seeds. By KROCKER (*Bied. Centr.*, 1881, 208—209).—The seeds of various species of plantain are used in Germany as cattle fodder, and with good results when ground and mixed with a little rye and clover hay. The author's analyses of two species, *Plantago lanceolata* and *P. major*, show such differences in composition, that he recommends care in the purchase of the most useful variety of the articles.

	<i>P. lanceolata.</i>	<i>P. major.</i>
Moisture.....	13·080	8·250
Protein matter	12·879	18·790
Fat.....	4·685	9·800
Non-nitrogenous extract	42·712	38·930
Cellulose	23·576	19·230
Mineral matter.....	3·068	5·000
	<hr/>	<hr/>
	100·000	100·000

J. F.

Effect of the Moisture in Soils on Yield of Potatoes. By BIRNER (*Bied. Centr.*, 1881, 154—155).—To ascertain the influence of moisture on the yield, 20 vessels were filled with the same kind of garden soil, each containing 7 kilos.; they were arranged in 5 series of 4 each, and so ordered that each contained a different percentage of moisture, being in other respects treated exactly alike. They ripened in the order of the vessels containing the largest proportion of water first, that containing least moisture not till 18 days after the first. The difference of produce was enormously in favour of the tubers planted in the moister parcels of soil, and the author thinks that when the necessary plant food is present, the dampness of the soil exercises a very decisive influence. J. F.

Utilisation of Diseased Potatoes. (*Bied. Centr.*, 1881, 212).—The damaged tubers, even if badly attacked, can be used as cattle food. They are best cut up small, boiled or merely scalded, mixed with chopped straw or chaff, and stored in narrow trenches covered up with clay: so stored they will keep many years; if steamed they should be kept in casks, as there is more adhering moisture; if not convenient to heat them as recommended, they should be sold at once to the distiller. J. F.

Prevention of Rot in Potatoes. By ROHL and G. v. HESS (*Bied. Centr.*, 1881, 212).—The tubers, whether sound or diseased, when taken from the ground, are left in a weak solution of calcium chloride, 1 part to 1,000 of water, for half an hour; they are then

transferred to a soda solution of the same strength, after which they are washed in clean water, and air dried— $\frac{1}{2}$ a kilo. of calcium chloride and the same quantity of soda is sufficient for 250 kilos. of potatoes.

J. F.

Money Value of Feeding Stuff. By J. KÖNIG (*Bied. Centr.*, 1881, 188—190).—At the Congress of Naturalists held at Cassel in 1878, a commission was appointed to try if a common basis of valuation of fodder materials could be arranged. Many analyses of various foods were compared and statistics of the minimum, maximum, and average prices for a series of years obtained from most of the German Chambers of Commerce. The prices vary very considerably, and the value attached to each ingredient constantly changes, so that the commission think an annual readjustment of the scale necessary. The author, however, suggests that if a relative value were assigned to the different nutritive components, it would be easy to make an approximate money valuation—for example, if protein, fat, and non-nitrogenous extract bore the relative values of 3:3:1, and the selling price were given, the money values could be determined. The subject is still under investigation, no positive results having been arrived at.

J. F.

On Salt-bush and Native Fodder-plants of New South Wales. By W. A. DIXON (*J. Roy. Soc., N.S.W.*, 14, 133—143).—The following table exhibits the proximate composition of a number of Australian fodder-plants belonging to the natural order *Chenopodiaceæ*. Like most plants of this order, they contain a very large proportion of mineral constituents; and the author remarks that he can find only one European plant of the same genus, viz., *Atriplex verrucifera*, from the Kirghis Steppes, which contains as much as 12·5 per cent. of ash, whereas in these Australian specimens the percentage of ash ranges from 24 to 31·8; in species of other genera of the same order, indeed, *Salsola*, for example, it sometimes rises to 30—42 per cent.*

The order in which the salt-bushes proper are considered from a grazier's point of view is: 1. *Atriplex numularia*, or Old Man's Salt-bush; 2. The Dwarf-Salt-bush, the others being regarded as inferior. The Cotton-bush is much valued, both from the fact that sheep get fat upon it, and from its ability to withstand long-protracted drought. The Blue-bush (*Kochia*) is not much liked by sheep, probably on account of its flavour, as it appears to have nearly the same nutritive value as the salt-bushes.

A comparison of the composition of these salt-bushes with that of well-known European fodder-plants,† shows that the former stand in a good position as regards their nutritive value. Table II exhibits the ratios in which the total ash, the common salt, and the potash, stand in relation to the total digestible matter taken as 100, including the oil, carbohydrates, and albuminoids. The average composition of the salt-bushes is also given, omitting the blue-bush, as the analysis of that plant was made on a specimen at an imperfect stage of growth, and the cotton-bush, as it is a plant of a totally different character.

* Gobel: see *Watts's Dictionary of Chemistry*, 1, 476: 5, 176.

† See *Watts's Dictionary of Chemistry*, 7, 530.

TABLE I.—Composition of Australian Fodder-plants.

	1. <i>Atriplex speciosa</i> . Dwarf salt-bush	2. <i>Atriplex campanulata</i> . Small salt-bush.	3. <i>Atriplex speciosa</i> . Salt-bush weed.	4. <i>Atriplex speciosa</i> . —	5. <i>Atriplex speciosa</i> . —	6. <i>Kochia pyramidata</i> . Blue-bush.	7. <i>Atriplex nummularia</i> . Old man salt-bush.	8. <i>Chenopodium bicornis</i> . Cotton-bush.
Oil	2.94	2.24	2.08	2.28	1.56	2.14	2.18	2.88
Carbohydrates ..	40.96	43.47	43.19	43.64	38.70	32.63	42.85	56.03
Albuminoids ..	14.68	12.25	13.37	12.68	16.18	19.94	16.45	9.18
Woody fibre....	15.60	18.12	14.88	14.44	14.48	8.04	7.24	24.91
Ash, CO ₂ ,	25.82	23.92	26.48	26.96	29.08	37.25	31.28	7.00
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Nitrogen.....	2.35	1.96	2.14	2.19	2.59	3.19	2.63	1.47
Woody parts ..	37 per cent.	8 per cent.	4 per cent.	46 per cent.	48 per cent.	37 per cent.	10 per cent.	6 per cent.
Edible.....	63 "	92 "	96 "	54 "	52 "	63 "	90 "	94 "
Ash Analysis.	On ash. On plant.	On ash. On plant.	On ash. On plant.	On ash. On plant.	On ash. On plant.	On ash. On plant.	On ash. On plant.	On ash. On plant.
K ₂ O	21.18 5.47	13.61 3.25	20.21 5.25	29.38 7.92	26.54 7.72	12.39 4.62	15.69 4.91	24.73 1.73
Na ₂ O	49.34 12.74	26.22 6.27	40.82 10.81	23.56 6.35	32.29 9.39	34.43 12.83	29.57 9.25	20.17 1.41
NaCl	2.31 0.60	35.36 8.46	7.95 2.10	12.46 3.36	6.21 1.80	26.67 9.93	30.28 9.47	8.24 0.58
CaO	12.74 3.29	8.47 2.03	14.56 3.96	15.47 4.17	14.56 4.24	8.75 3.26	8.65 2.71	24.33 1.70
MgO	4.83 1.25	5.82 1.39	5.13 1.36	6.96 1.88	6.60 1.92	7.32 2.72	6.77 2.12	8.27 0.58
Fe ₂ O ₃	0.73 0.19	1.83 0.44	0.92 0.24	1.21 0.33	1.65 0.48	1.28 0.48	0.64 0.20	1.28 0.09
SO ₃	4.43 1.14	2.62 0.63	2.57 0.68	1.01 0.27	3.57 1.04	1.11 0.41	3.17 0.99	3.95 0.28
P ₂ O ₅	2.80 0.72	3.80 0.91	4.41 1.17	3.44 0.93	4.21 1.22	3.98 1.48	4.11 1.28	5.44 0.38
Silica, soluble ..	1.64 0.42	2.27 0.54	3.43 0.91	6.51 1.75	4.37 1.27	4.07 1.52	1.12 0.35	3.59 0.25
	100.00 25.82	100.00 23.92	100.00 26.48	100.00 26.96	100.00 29.08	100.00 37.25	100.00 31.28	100.00 7.00

TABLE II.—*Ratios of Digestible Matter, of Ash, Potash, and Salt.*

	Digestible.	Ash.	KOH.	NaCl.
1. Dwarf salt-bush	100	44	7·417	1·024
2. Small salt-bush	100	41	5·607	14·590
3. Salt-bush-weed	100	45	8·952	3·581
4. Salt-bush	100	47	13·516	5·734
5. "	100	53	13·751	3·207
7. Old Man salt-bush.....	100	51	7·986	15·403
	100	47	9·538	7·689
8. Cotton-bush.....	100	10	2·541	0·847
Meadow hay.....	100	12	3·207	1·604
Red clover	100	10	3·524	0·720
Lucerne.....	100	12	1·969	0·581
Oaten hay.....	100	8	3·277	0·863

These salt-plants are used chiefly for the pasturage of sheep, and for this purpose they are well adapted by their large amount of soluble chlorides, which, by evolving hydrochloric acid in the stomach, or rather in the gastric juice, enables the animals to digest considerable quantities of cellulose. The large proportion of potassium salts contained in them is moreover favourable to the abundance and richness of the wool, inasmuch as the greasy substance called "suint," which constitutes about a third of the weight of merino wool, and about 14 per cent. of ordinary wool, consists of the potassium salt of a peculiar organic acid.

H. W.

Cultivation of Various Agricultural Plants. By J. SAMEK (*Bied. Centr.*, 1881, 471—473).—A report concerning the cultivation of various farm crops in South Tyrol; of purely local interest.

E. W. P.

Rotation of Crops in Kitchen Gardens. (*Bied. Centr.*, 1881, 212.)—Where manure is abundant, gardeners are in the habit of fully manuring half their garden yearly; but it would be more economical, and according to the author, quite as successful a plan to manure only one-third each year, and pursue a three years' system of rotation, viz., in the freshly manured portion sow the exhausting plants, such as cabbage, salads, scorzonera, horseradish, common radish, leeks, celery, cucumbers, parsley, endive, &c. In the second portion, that which was manured the previous year, cultivate the less hungry crops, which require a good soil, but little manure, white, yellow, and red beet, potatoes, &c.

In the third portion should be cultivated the so-called "lean" vegetables, which thrive better on poor than rich soils, viz., beans, peas, lentils, and onions.

J. F.

Researches on Phylloxera. By VALÉRY-MAYET and others (*Bied. Centr.*, 1881, 474—479).—The egg of the phylloxera is to be

found on those young American vines, whose leaves bear galls, and the egg may be looked for under the bark of two- or three-year old wood. Lichtenstein having found the egg in the two-year old wood which is left after pruning, considers the barking, &c., of the vines as useless, as the phylloxera is not on the stem. The want of retention of water by sandy soils is, according to St. André, the reason why vines growing on sandy soils are more able to resist the attacks of this pest. Gesmon thinks that infected vineyards should be left to themselves, nothing being done beyond pruning. Macagno introduced into the soils by holes 50 and 25 cm. deep, 88 and 66 grams carbon bisulphide per square meter; eight days sufficed to kill the insects. C. Bourdin proposes to destroy the phylloxera by introducing carbon bisulphide vapour into the soil; this plan was, however, proposed in 1880 by v. Babo. F. de Savignon describes five varieties of vines indigenous to California.

E. W. P.

Black Earth of Russia. By C. SCHMIDT (*Bied. Centr.*, 1881, 364—368).—The samples of soil, fifteen in number, varied from ferruginous clay to limestone. The percentages of ferric oxide varied from 2.0 to 6.0; of alumina from 6.6 to 19.6; of humus from 1.4 to 15.4; and of phosphoric acid from 0.095 to 0.257; and of nitrogen from 0.086 to 0.775; the amount of the latter varying almost constantly with the percentage of carbon. Chlorine and sulphuric acid were present in only very small quantities. The following mean results were obtained from the eleven non-calcareous samples dried at 100°:—

	Total.	Extracted by cold 5 p.c. HCl.	Not extracted by the former, but by hot 10 p.c. HCl.	Not extracted by hot 10 p.c. HCl.
Water expelled at 150°	3.005	—	—	—
Dry humus	9.025	—	—	—
Potash	1.880	0.116	0.564	1.200
Soda	1.205	0.031	0.092	1.082
Lime	1.305	1.135	0.097	0.073
Magnesia	1.562	0.275	0.941	0.346
Ferric oxide	3.816	0.551	2.887	0.378
Alumina	14.332	1.470	5.782	7.070
Silica	55.885	3.773	12.780	39.322
Quartz and rutile	6.475	—	—	6.475

The lime dissolved out by cold 5 per cent. HCl, existed probably in combination with humus and as some easily decomposable zeolite: the alumina extracted by cold acid was probably present as allophane. The bodies brought into solution by hot 10 per cent. HCl may be set down as zeolites and feldspars, and silicates of the kaolin group, whilst the insoluble residue consists of potash and soda feldspars mixed with quartz sand. Only small quantities of mica, hornblende and rutile were observed (compare p. 456).

J. K. C

Permeation of Water through the Soil. By A. ANDOYNAUD and B. CHAUZIT (*Bied. Centr.*, 1881, 217—220).—In a former paper the authors have shown that about one-fourth of the downfall drains through a stratum of soil one and a-half meters in depth. One litre of the drain-water contained on the average 0·868 gram of solids. The object of the present investigation was to ascertain the composition of the dissolved matter. From January 1st to March 18, the drainage-water from the boxes of earth of 5·88 sq. meters surface amounted to 500 litres, the downfall being 2,400 litres. Little more than one-fifth had therefore permeated the soil, and this was probably due to the sinking of the earth in the boxes. On three occasions the drainage water was analysed with the following results:—

	Mgram. per litre.		
	February 27.	March 6.	March 12.
Silica and organic matter.....	3	48	46
Calcium carbonate	73	86	102
Other earth carbonates.....	51	27	20
Potassium sulphate	192	198	194
Calcium „	48	39	70
Magnesium „	24	0	21
Potassium nitrate	47	45	35
Sodium chloride.....	337	389	344

J. K. C.

Investigations on Warmth in Soils. By VAN LIEBENBERG (*Bied. Centr.*, 1881. 148—154).—A soil becomes heated in proportion to its absorptive power, and retains heat the longer as its emissive power and conductivity is smaller, and specific heat greater. The specific heat of any sample of soil, as compared with another by weight, depends much on the moisture contained in it, but chiefly on the amount of humus or organic matter which that body contains; with tilled soils this is specially the case. When, however, estimations are made by volume, which mode the author prefers, the difference in favour of soils rich in humus is not so evident.

The emission of warmth was measured by Melloni's apparatus, and from his experiments the author believes that heat is emitted chiefly from rough and coarse particles of earth only, and that in cultivated ground where such coarse pieces are carefully broken up or surrounded by finer particles, the rate at which heat is emitted is the same at like temperatures for all descriptions of air-dried soil. Warming and cooling of soils formed the next series of experiments, and the author found that as a rule dark-coloured samples became warmer quicker than those of lighter colour, and of the darker ones, those of less specific heat warmed the most rapidly. In the operation of cooling, this difference due to colour was not perceptible, the soils with the smallest heat capacity cooled most quickly, except such as contained large quantities of organic matter, this appearing to retard the emission of heat. Dry soil becomes warmer much quicker than damp, but the latter retains the heat much longer.

The author concludes with some practical advice to farmers. He

says that the use of animal manure is rational and beneficial, as it adds to the soil those organic substances which help to form humus, and impart the useful dark colour which attracts and retains heat. The drainage of the soil he considers of even more importance as regards temperature. Wet soils are slow to absorb heat, and the specific heat is low, delaying the fructification of plants and causing late seasons, sickly plants, and crops deficient both in quantity and quality. With well-drained land, the earliest heats of spring are at once absorbed (and retained longer by the organic matter); the seeds germinate early, the young plants develop quickly, and the course of vegetation is normal. J. F.

Potash Salts as a Manure. By F. FARSKY (*Bied. Centr.*, 1881, 451).—The experimental crops were: wheat, rye, barley, oats, buckwheat, potatoes, and sugar-beet. Unless the land is wet, potash salts always produce better crops, even when sown with the seed. The beneficial action is more assured if phosphates or nitrogenous manures are added.

Potassium chloride is better than the sulphate, both as regards the quantity and quality of the yield. The method of manuring is to mix the salt with the seed. Potash salts, and especially the chloride, accelerate the ripening by 7—14 days. Potash salts also cause the soil to retain more moisture. An addition of lime, or lime and superphosphate to the chloride is of great advantage. E. W. P.

Manuring Experiments with Phosphoric Acid in Different Combinations. By FITTBOGEN and others (*Bied. Centr.*, 1881, 156—162).—The first series of experiments relate to the suitability of different combinations of the acid in soluble and insoluble forms for cultivation of plants in sand. A number of pots were filled with quartz sand previously ignited and treated with hydrochloric acid to remove humus and lime. To one half the number a quantity of phosphatic manure equivalent to 142 mgrms. of phosphoric acid was added, and to the other half double that quantity. In each pot 6 plants of barley were then planted. Omitting details, the dry substance in the crop yielded the following percentages, together with which is given the contents of the manures in phosphoric acid:—

	Phosphoric acid.			Percentage yield after	
	Total.	Sol. in water.	Sol. in citrate amm.	lesser quantity.	Double quan.
Mejillones guano superphosphate.....	21·71	19·48	1·73	32·2	65·1
Lahn phosphorite superphosphate.....	18·84	4·13	5·83	12·0	23·3
Precipitated calcium phosphate.....	28·56	—	6·36	8·1	7·9
Kladno phosphate (aluminium phosphate).....	11·36	—	66·8	9·7	10·7
Chemically pure ferric phosphate.....	—	—	—	10·4	11·7
Without phosphoric acid ..	—	—	—	—	9·8

It will be seen that increased quantities were useful only in the cases of the superphosphates containing phosphoric acid soluble in water. The author concludes that chemical action is more useful than mechanical subdivision and admixture; and that the roots of plants do not possess the power of directly assimilating the phosphoric acid from insoluble combinations.

Field trials were made on oats and potatoes with the same manures. In one series phosphates alone were used, in another a quantity (not stated) of ammonium sulphate was added. The results were decidedly in favour of the latter, both with oats and potatoes. The author believes the phosphates to have remained inactive, and that the ammoniacal manure was the effective agent.

At the experimental station of Kiel, trials were made with oats manured with precipitated calcium phosphate, Estremadura superphosphate, steamed bones and dissolved bones. The superphosphate gave a heavier crop both of corn and straw than the precipitated phosphate, and dissolved bones than the steamed bones, but the author says that the latter will be found effective the following season.

At Renow-Dombrowo in Posen, experiments were made with different manures on potatoes. The soil was about 12 cm. deep, resting on a sandy subsoil, with large stones and marly loam beneath. Part of the manure was ploughed in with a subsoil plough, and the rest applied as top dressing. The relative yield was as follows; the plots contained each 1 morgen:—

			Potatoes.
No. 1.	2 centners Chili saltpetre		45 centners
2.	1 " " and 2 centners nitro- phosphate		46 "
3.	1 " " and 2 centners bone- black superphosphate	48	"
4.	1 " " and 2 centners retro- graded phosphate ..	50	"
5.	Unmanured, deeply cultivated.....	32	"
6.	" cultivated in ordinary way.....	24	"

The result of the retrograded phosphate is remarkable.

At Birner Regenwald experiments were made in growing potatoes with various phosphates, with and without the addition of nitrogenous manures. The most successful was a combination of Mejilones superphosphate with ammonium sulphate; the least was that in which Lahn superphosphate was used. J. F.

Relative Value of Soluble and Insoluble Phosphates as Manure. By M. MAERCKER (*Bied. Centr.*, 1881, 378—389).—In each of these experiments the land was divided into four lots:—lot 1 was unmanured, lot 2 was manured with nitrogen (in form of ammonium salts or nitrates), lot 3 with nitrogen and soluble superphosphate, and lot 4 with nitrogen and insoluble phosphates. The nitrogen was generally applied as Chili saltpetre, only in a few cases being given as ammonium sulphate; the soluble phosphoric acid used being in the

form of "Baker" or Mejillones guano superphosphate. As more insoluble phosphates the following were used—(1) precipitated calcium phosphate (bye-product in the manufacture of glue), containing 32 per cent. of phosphoric acid, of which 29 per cent. was soluble in ammonium citrate; (2) kladnophosphate (an aluminium phosphate from iron foundries) with 20·04 per cent. phosphoric acid; (3) retrograde superphosphate from lahnphosphorite, with about 10 per cent. phosphoric acid, of which two-thirds was soluble in water, and the remainder in citrate solution; (4) so-called half-phosphate, or Baker guano treated with just enough sulphuric acid theoretically to produce only dicalcium phosphate. In reality only a small quantity of the latter compound is formed, whilst part of the material is converted into acid calcium phosphate, and the remainder left untouched. The preparation in question contained 21·4 per cent. phosphoric acid, of which 10·6 was soluble in water, 5·2 in citrate, and the remainder insoluble.

(1.) *Precipitated Calcium Phosphate*.—Experiments were tried on barley, oats, peas, beans, potatoes, and beetroot. In 12 of the 16 experiments with barley, the phosphates gave a greater yield than salt-petre alone; of these 12, two were carried out in sandy soil, two in sandy loam, and eight in good loam specially adapted for barley. The mean results in kilos. per hectare are given in the following table:—

	Fruit.				Straw and Chaff.			
	Unmanured.	Chili saltpetre.	Do. with precipitated calcium phosphate.	Do. with superphosphate.	Unmanured.	Chili saltpetre.	Do. with precipitated calcium phosphate.	Do. with superphosphate.
Sand.. .. .	1,452	1,564	1,789	1,694	1,757	2,064	2,428	2,174
Sandy loam.. . . .	2,227	2,316	2,910	2,807	2,812	3,078	3,669	3,668
Loam.. . . .	2,219	2,239	2,772	2,762	2,935	3,308	3,484	3,555

On the real barley soils, therefore, precipitated phosphate appeared to be of equal value with superphosphate, whilst on thin sandy soils the latter appeared to possess a slight advantage. In the case of oats, 12 experiments out of 18 showed an increase by the use of phosphoric acid. Here the results were reversed, as the precipitated phosphate was somewhat superior to superphosphate on sandy soils, and almost equal in value on loam; it was noticed that better results were obtained without the use of a nitrogen manure. The experiments with peas and beans were so affected by bad weather as to be of no value. The potatoes were also grown under very unfavourable conditions, but 11 experiments were completed; in these the superiority of precipitated phosphate in the lighter soils and of superphosphate in the heavier was established. In the case of beetroot no special results were obtained, each form of phosphate having similar effects. On the whole, therefore, precipitated calcium phosphate appeared to

give as good results as soluble phosphate, especially in lighter soils; this may be partly owing to the fine state of division of the former, by means of which it could be intimately mixed with the soil.

(2.) *Kladnophosphate*.—In two experiments with barley on black fenny soil, the kladnophosphate was found to be of the same value as superphosphate, whilst the former proved rather superior in the case of oats grown on a heavy soil rich in lime, and inferior when applied as manure to potatoes; in this respect the same occurred as in the case of precipitated calcium phosphate.

(3.) *Retrograde Phosphoric Acid*.—In many cases this was found to be equal to soluble superphosphate; this result may of course be possibly due to the percentage of soluble phosphate present in the former. At any rate this phosphate cannot be ranked as high as precipitated calcium phosphate, as it is not nearly so fine in the grain, and does not allow of such intimate admixture with the soil. The experiments, however, on this head are not sufficiently numerous to give a permanent definition of the value of retrograde lahnphosphorite.

(4.) *Half-phosphate*.—As before stated, this contains very little dicalcium phosphate, consisting chiefly of acid and basic calcium phosphates. In many cases, however, half-phosphate was the equal of superphosphate, a result which may be taken to imply that very often a smaller quantity of soluble phosphate would suffice for the required end.

J. K. C.

Manuring Experiments to determine the Value of Phosphoric Acid soluble in "Citrate" Solution. By E. WOLFF and others (*Bied. Centr.*, 1881, 435—450).—These experiments, carried out in various parts of Germany and on various kinds of soil, were made to estimate the value of "reduced" phosphate as compared with soluble phosphate. The superphosphates employed were a Mejillones superphosphate, containing 18·6 per cent. soluble, and a trace of insoluble phosphate, and a phosphorite superphosphate, containing 4·4 per cent. of soluble and 4·0 per cent. of reduced phosphate: each plot received 20 kilos. per morgen of "assimilable" phosphoric acid. The crops were oats. In some cases experiments were also made in plants grown in boxes 25 cm. broad, and containing 17·5 kilos. soil. Wolff reports from Hohenheim that the Mejillones "superphosphate" produced a crop double of that produced by phosphorite. The crops grown in boxes showed the same result, that in a soil containing little or no lime or humus "reduced" phosphate is of little value.

J. König reports from Westphalia the results of 16 sets of experiments made in six plots per morgen; when (2) bone-meal, (3) precipitated tricalcium phosphate, (4) precipitated dicalcium phosphate, (5) "reduced" lahnphosphate, (6) and Mejillones superphosphate were employed; (1) was unmanured. Ammonium sulphate was also added to 3 and 6. The amounts of phosphoric acid and nitrogen added varied very considerably. Here the nature of the soil varied greatly, and the crops were oats, potatoes, and meadow grass. From several causes the results are not quite trustworthy, but

in general it has been found that soluble phosphates on heavy and reduced phosphates on light and sour humous soils are advantageous.

Holdefleiss in Silesia compares the action of Chili saltpetre with ammonium sulphate, and also soluble with reduced phosphates, on oats, barley, and sugar-beet on various soils, and finds that saltpetre, even at the high price of 18 M. per centner, is of value to oats on humous, limey, clay soils. It is also of most value when the crop is barley upon a soil similar to the foregoing; that phosphates even on a rich, well-cultivated land are of value, and that steamed bone-meal is of like value as superphosphate, owing to the rapidity of its decomposition. For sugar-beet on a rich alluvium Chili saltpetre is better than ammonium sulphate, especially when acting together with phosphoric acid; dicalcium phosphate appears to be equivalent to monocalcium phosphate. On very rich soils, there is no advantage gained by manuring sugar-beet. During a bad season potatoes do not profit much by manure; Chili saltpetre is, however, active, and dicalcium phosphate is not behind superphosphate in value. On light sandy soils sulphate of ammonia is better than sodium nitrate, and reduced than soluble phosphate. On an alluvial soil, newly brought into cultivation, only the most soluble forms of nitrogen and phosphoric acid produce a gain. From the experimental station in East Prussia it is reported that nitrogen alone reduces the yield of sugar in beet, but that the quality is improved if phosphoric acid is also added at the same time. The ripening of barley when grown in boxes is accelerated by nitrogenous or phosphatic manures, and on the whole soluble phosphate is found to be best. Siewerts, in West Prussia, finds that as regards the weight and quality of a potato crop, stable manure is the worst manure, and soluble phosphates do not produce a higher result than Chili saltpetre alone, or in combination with precipitated phosphate. Reports also from Dietrich and Henneberg are published, but as their results are dependent on the peculiarities of the local soils they are of little general interest.

E. W. P.

Gypsum as Manure. By NANQUETTE and others (*Bied. Centr.*, 1881, 162—163).—The author has for many years experimented with this substance on pasture lands, and finds it decidedly beneficial, especially when used in the autumn, and believes that even on lands rich in lime its use would be found very profitable. Medicus recommends German farmers to employ it to grow fodder and vegetables. Sch, while unable to account for its action, agrees with the other observers, and points to its use as a preservative and absorbent for the ammonia in stable manure; the low price of the article, he thinks, should lead to its extended use. Refuse gypsum should be tested as to its manurial value before purchase.

J. F.

Money Value of Stable Manure. By E. LECOUTEUX (*Bied. Centr.*, 1881, 177—178).—The author having had the manure from 32 horses, 3 cows, and 12 swine analysed for 4 years, found from a calculation of the value of the ingredients that 1,000 kilos. were value for 18.91 marks, but as the manure is not exhausted till the end of

four years, 3 years' interest is deducted, making the value 16·07 marks at the place of production. J. F.

Lake Mud and Marsh Earth as Manure (*Bied. Centr.*, 1881, 207—208).—The lands on which these manures are most profitably employed are light porous soils, which are neither too wet nor too dry, also well drained, and boggy soils which have been partially reclaimed; and on boggy land which has not been tilled; the latter should be previously harrowed and lightly burned. Mixed with sand, it is spread in heaps on the fields, and left over some months to ripen under the influence of the weather, when it falls into powder, and is spread as a top dressing, or ploughed into the soil. The quantity employed should be large, the amount per morgen should not be less than 25,000 kilos. (morgen = 0·63 acre); but where cost of transport is not great larger quantities should be used. The employment of these materials does not altogether supply the place of manures, which are to be employed with them and in smaller quantities, the apparent effect of the combination being to prolong and improve their action. Various crops have been grown advantageously with their assistance. J. F.

Ground Wood as Horse Litter (*Bied. Centr.*, 1881, 208).—This material is coming into extensive use in America; it is finer in grain than sawdust, has greater absorptive power, prevents loss of ammonia, and consequent injury to the saddlery; it affords a more comfortable footing to the horse, and the resulting manure is of greater value than that from straw or sawdust. J. F.

Manuring Experiments on Oats. By H. GAUDICH and others (*Bied. Centr.*, 1881, 452).—On three farms in Saxony experiments were instituted to determine whether spring barley should be manured by spreading, and then harrowing in the manure, or whether the manure should be ploughed in. The manure consisted of a mixture of 6 kilos. nitrogen as Chili saltpetre, and 6 kilos. soluble phosphoric acid per half acre (Saxon). On one plot this mixture was ploughed in 10 cm. deep, on another it was only harrowed in, and the third was left unmanured. Andreä, using a fourth plot, top-dressed it with the same mixture, and treated a fifth with sulphate of ammonia instead of saltpetre, like plot 2. The results for 1879 only are given, as in 1880 the season was bad. It was found best to plough in the manure, the smallest yield being produced by top dressing. The ammonium sulphate was not so good a manure as the saltpetre, and ought to have been applied earlier. E. W. P.

Manuring Experiments with Summer Barley. By A. ZOEBL (*Bied. Centr.*, 1881, 175—176).—These experiments were made at the experimental station of Neutitschein in Austria, in a mild clay soil with a porous subsoil; the previous crop was potatoes, and it was arranged that the cost of each description of manure employed should be as nearly as possible the same; the manure was harrowed in the day before the sowing.

The most successful in the production of the grain was nitrophosphate alone, a mixture of Baker guano superphosphate with potassium sulphate and dissolved bones, so that the phosphoric acid appeared most effective. Potash ranked next. The nitrogen in the bone-meal appeared more useful than in the ammonium salts; the greatest weight per hectolitre, however, was found in the unmanured parcels, although falling below the total yield of the manured plots.

J. F.

Manuring Experiments with Potatoes. By H. TAPPENTHAL and others (*Bied. Centr.*, 1881, 171—173).—This paper is a collection of reports from different agricultural experimental stations. The first presents in tabular form the results of six experiments in which the kind of potato was in each case the same, and the manures different; the best effects were produced by the use of 1 part of superphosphate with half the quantity of sodium nitrate, the next best by superphosphate alone. Kainite produced a large weight of the tuber, but the percentage of starch was lower than that of any other of the plots. A second series of experiments relates to the employment of different quantities of sodium nitrate, and the results were decidedly in favour of the smallest quantity employed, $\frac{1}{2}$ centner per morgen, the employment of $\frac{3}{4}$ and of a whole centner adding materially to the cost of the manure, and showing a money loss when compared with an unmanured plot.

The third class of experiments relates to the employment of dissolved guano, stable manure, and superphosphate on plots of good rye growing soil; the experimenter gives preference to superphosphate containing nitrogen, called in commerce nitrophosphate, as producing the centner of potatoes at the lowest cost.

The last table given compares the results of bone-meal, sodium nitrate, and stable manure on two varieties of potato; a mixture of 1—12 sodium nitrate and bone-meal appears to have yielded the largest crop.

J. F.

Manuring Potatoes. By H. TIEDE (*Bied. Centr.*, 1881, 455).—The author concludes that for potatoes organic manures are far preferable to those of mineral origin; also that the addition of the former class of manures greatly aids the action of the latter.

E. W. P.

Manuring Experiments with Sugar Beets. By M. MÄRCKER (*Bied. Centr.*, 1881, 163—170).—A summary of the second year of an exhaustive course of experiments on various points connected with the most profitable mode of manuring beet. The plan on which the experiments was conducted is given in this paper; it was to divide amongst 36 farmers seeds suitable to their different soils, and cause their cultivation to be carried on under the superintendence of the author, who compared and tabulated the results. The experiments were arranged so as to compare the effects of Chili saltpetre and ammonium sulphate, the effect of organic manures containing nitrogen, the effect of strong doses of phosphatic manures, and a comparison of the values of soluble and insoluble phosphates; two of these series of experiments are not reported on.

Chili saltpetre was used in quantities of 1, 2 and 3 centners per morgen, the effect of 2 centners was much greater than the smaller quantity, and in some cases the 3 centners per morgen yielded a profitable return, but on the average the 2 centners appeared to satisfy the requirements of the roots, although cases might occur when even a larger quantity might be useful.

Ammonium sulphate operated less favourably than the Chili saltpetre in a long course of experiments, but the differences were not so striking as to induce the author to recommend farmers to discontinue its use where it had been found serviceable. The different times of year when these manures were applied gave no decisive results; the author believes than an application early in spring is the best for Chili saltpetre, and autumn for the ammonium sulphate.

The use of phosphatic manures, in conjunction with Chili saltpetre, increased the quantity and improved the quality of the roots, and the author thinks that farmers would be wrong to continue the use of nitrogenous manures alone, the proportion between the two must be settled by future experiment, but 2 parts of the Chili saltpetre to 3 parts of superphosphate yielded very excellent results. In conclusion, the author gives a summary of experiments made on heavy manuring with Chili saltpetre, in which the sugar contents and quotients of polarisation are not *decreased* by excessive use of this manure, but there is not sufficient increase to pay the extra cost of the manure; the use of increased quantities of superphosphate, however, does materially increase the quotient.

As all the experiments were made in the one district, modified results might follow similar ones made in other soils. J. F.

Comparative Manuring Experiments. By C. NERGER (*Bied. Centr.*, 1881, 174—175).—The experiments were undertaken to ascertain what nutritive matter a certain soil was deficient in; they consisted in sinking a number of boxes in a field, filling them with the soil which had been dug out, and after manuring each two boxes alike, sowing them all with barley. The plan of manuring was to supply all the constituents of the ash of the plant in as nearly exact proportions as found on analysis, but to leave out of each pair of boxes some important ingredient, such omission being different in each pair; for example, in one case magnesia was omitted, in another phosphoric acid, in another chlorine, and so on. The highest results were obtained from the addition of nitrogen to the complete manure, the lowest from the use of the complete manure minus silicic acid; from this the author infers that the soil in question is deficient in this particular ingredient. He recommends his plan to practical farmers, to enable them to learn the nature of their own soils, as he thinks there is a great deal of money wasted by the employment of unsuitable artificial manures, and that the choice of a manure has more influence on the crop than weather. The editor in a foot note warns them against such a conclusion, as experiments of this class cannot be carried out with sufficient accuracy to insure absolute certainty.

J. F.

Manuring Experiments. By J. F. PETERS (*Bied. Centr.*, 1881,

453).—Because a field manured with Chili saltpetre yielded in the next year a good crop, the author considers that this manure does not impoverish the land to the extent generally supposed. Ten plots were manured with various phosphatic manures, some in equal money value, others in equal “phosphoric” value; two plots received only saltpetre and ammonium sulphate as top dressing. The crop being oats, it was found that the saltpetre produced the highest yield, and the ammonia manuring was also highly beneficial. Phosphates alone were much less active.

E. W. P.

Analytical Chemistry.

Separation and Estimation of Nitric and Nitrous Acids.

By A. PICCINI (*Gazzetta*, 1881, 267—274).—The author has already suggested an easy method of detecting small quantities of nitric acid in presence of excess of nitrous acid, founded on the different reactions of these acids with urea (this Journal, 1880, Abstr., 139); and he now finds that normal ferrous salts may be used for the same purpose, inasmuch as they turn brown on addition of a nitrite, especially when heated and in concentrated solution, or in a solution acidulated with acetic acid, whereas they exhibit no such reaction with nitrates. If therefore a neutral ferrous solution be placed in contact with a mixture of nitrates and nitrites and heated, the nitrite will be decomposed, with evolution of nitrogen dioxide, which will colour the liquid brown, while the nitrate will remain unaltered, until a strong acid is added, which liberates the nitric acid and exposes it to the reducing action of the ferrous salt. If the decomposition of the nitrite under these circumstances is complete and takes place in the manner above indicated, the quantity of gas evolved while the solution remains neutral will afford a measure of the amount of nitrous acid present; and that which is given off after the acidulation of the liquid will give the measure of the nitric acid.

In applying these reactions to analytical purposes, the author finds that ferrous chloride is preferable to the sulphate, as it acts more rapidly, and being also more soluble than the sulphate, it enables the operation to be carried on with smaller quantities of liquid. To obtain a perfectly neutral solution of ferrous chloride, iron filings are digested first at ordinary then at a higher temperature, with hydrochloric acid of sp. gr. 1.12 in a flask filled with carbonic acid, and when the iron is no longer attacked, an excess of moist, thoroughly washed ferrous oxide is added, and the liquid is boiled and afterwards left to cool in the atmosphere of carbonic anhydride; a few drops of pure dilute soda solution are then added, whereby a precipitate is formed, and the liquid, after agitation, is filtered also in carbonic acid gas. In this manner a deep green solution of neutral ferrous chloride is obtained, which may be preserved in an apparatus similar to that used by Fresenius for keeping stannous chloride.

For the description of the apparatus employed and the details of the analytical operations, we must refer to the original paper; the results are very exact.

H. W.

Separation of Aluminium from Iron and Chromium. By A. CARNOT (*Compt. rend.*, **93**, 154—156).—This method is based on the fact that aluminium phosphate is practically insoluble in a boiling feebly acid liquid, even in presence of tartaric acid. To the hydrochloric or nitric acid solution of the mixed oxides, about 1 gram tartaric acid or potassium hydrogen tartrate is added, then ammonia and ammonium sulphide in excess. The precipitated iron sulphide is filtered off, and the iron estimated either gravimetrically or volumetrically: an excess of sodium phosphate is added to the filtrate, then a slight excess of hydrochloric acid to decompose the excess of ammonium sulphide, and from 4 to 5 grams sodium acetate. The liquid is afterwards boiled, kept at about 100° for one to two hours, and filtered. In order to remove tartaric acid, the aluminium phosphate is dissolved in dilute nitric acid, the solution almost neutralised with ammonia, a few drops of phosphoric acid and 2 to 3 grams ammonium acetate added, and the liquid again boiled. The gelatinous precipitate is washed with boiling water, and may be ignited without detaching it from the filter-paper. The solution should be somewhat concentrated, and as little wash-water should be used as possible, since the aluminium phosphate is not completely insoluble. Formates may be used instead of acetates, with equally good results. If neither formates nor acetates are added to the liquid, precipitation is still complete, but the precipitation is difficult to wash. The results are accurate.

If chromium is present, it must be converted into chromate by fusion with pure potassium hydroxide and nitrate, the fused mass dissolved in water, the solution slightly acidified with nitric acid, and the aluminium precipitated as above. An excess of aluminium nitrate is added to the boiling filtrate in order to precipitate the phosphoric acid, and the chromium is estimated in the filtered solution as lead chromate.

C. H. B.

Electrolytic Estimations and Separations. By A. CLASSEN and M. A. v. REIS (*Ber.*, **14**, 1622—1633).—Nickel, cobalt, iron, zinc, bismuth, copper, cadmium, and tin can be accurately estimated by the following process. Ammonium oxalate is added to the solution of the metal in sufficient quantity to form a double oxalate. The liquid is heated, and 4 grams of solid ammonium oxalate are added. The hot solution is then subjected to electrolysis, a piece of platinum foil of about 4.5 cm. across being used as the positive pole, and a deep platinum basin as the negative electrode. The deposited metal is carefully washed with water, alcohol, and finally with ether. Lead and arsenic cannot be satisfactorily estimated by this method.

In presence of potassium oxalate, manganese is deposited from solutions of its nitrate on the positive electrode as the dioxide. Since the deposit does not adhere firmly to the platinum, it is necessary to filter the liquid and convert the precipitate into Mn_2O_3 by ignition.

In order to estimate antimony, the metal is first precipitated by sulphuretted hydrogen, the free acid in the mixture is neutralised with

ammonia, and the precipitate dissolved in ammonium sulphide. The solution is then mixed with ammonium sulphate and electrolysed.

In the *separation of iron from manganese* by electrolysis, a large excess of ammonium oxalate must be employed in order to delay the precipitation of the manganese dioxide until the greater part of the iron has been precipitated. Should the liquid contain twice as much manganese as iron, free oxalic acid must be added to the mixture. In this separation, the best results are obtained by using the current from two Bunsen's elements. Since a small quantity of manganese escapes precipitation, it is necessary to throw down the manganese in the filtrate from the MnO_2 precipitate by the addition of ammonium sulphide.

Separation of Iron and Alumina.—The neutral or feebly acid solution is mixed with an excess of ammonium oxalate, and is electrolysed while hot. The current should be interrupted as soon as the iron is precipitated, in order to prevent alumina being deposited with the iron. The liquid decanted from the deposit of iron is boiled with ammonia to precipitate the alumina. If the ammonia is in excess, the precipitate formed during electrolysis must be dissolved by the addition of oxalic acid and reprecipitated by the current. W. C. W.

Separation of Nickel and Cobalt. By G. DELVAUX (*Compt. rend.*, **92**, 723).—The mixture of the two oxides or sulphides, free from all other metals, is dissolved in aqua regia containing much hydrochloric acid, largely diluted, and saturated with ammonia. Potassium permanganate is added until a persistent rose colour is obtained, and then the nickel with the manganese is precipitated by potassium hydroxide. The precipitate is washed, redissolved, and the process repeated.

The cobalt is precipitated from the mixed filtrates and washings acidified with acetic acid by sulphuretted hydrogen. The mixture of nickel and manganese oxides is dissolved in hydrochloric acid, ammonia added in excess, and the liquid exposed to the air. The manganese becomes oxidised, and is entirely precipitated. The nickel may then be precipitated by sulphuretted hydrogen.

The method gives very accurate results, and may be applied on the large scale. C. W. W.

Distribution of Arsenic in the Animal Body. By S. W. JOHNSON and R. H. CHITTENDEN (*Am. Chem. J.*, **2**, 332—337).—The body of a woman who had died of chronic poisoning with arsenious acid, was found, after having been buried for a year and a half, to contain 2.8463 grains of As_2O_3 , of which 2.8463 grains were contained in the internal organs—stomach, liver, lungs, brain, &c.—leaving 2.3798 grains for the muscle and bone tissues. These results differ considerably from those obtained by Scolosuboff (*Bull. Soc. Chim.* [**2**], **24**, 124; this Journal, **29**, 92), who, from experiments upon dogs poisoned slowly with solution of sodium arsenite added to their food, or quickly by subcutaneous injection of the same solution, concluded that the greater part of the arsenic becomes localised in the brain and other parts of the nervous tissue, and therefore that in cases of acute

arsenical poisoning the legal expert should search for the arsenic chiefly in the brain. Johnson and Chittenden, on the other hand, direct attention to the well-known fact that the form of the poison has a very decided influence on the rapidity of its absorption, and is likely also to modify the rate and amount of its absorption by different tissues: hence, as cases of poisoning by sodium arsenite are not of common occurrence compared with those in which the less soluble white oxide has been used, the deductions drawn from Scolosuboff's experiments are not applicable to the common forms of arsenical poisoning. Experiments on a large dog, to which 6.5 grams of solid As_2O_3 had been given in his meat for eight days, in doses increasing from 0.1 gram to 2.5 grams daily, showed that 100 grams of intestine gave 0.0020 of metallic arsenic, 100 liver gave 0.0010 As, 113 kidneys gave 0.0035 As, 100 muscle 0.0002 As; 150 urine in bladder gave 0.0003 As, whereas the entire brain yielded only a faint mirror, and 100 of blood a distinct mirror.

Similar results have been obtained by E. Ludwig (*Jahresb. für Tierchemie*, 1879, 85), who finds that in human beings as well as in dogs poisoned by arsenic, and in acute as well as in chronic cases, the liver contains the largest amount of arsenic, and the kidneys in acute cases contain a considerable quantity, whereas the bones and brain in either case contain only small traces.

H. W.

New Method for the Volumetric Estimation of Molybdenum. By F. MAURO and L. DANESI (*Gazzetta*, 1881, 286—293).—In examining some compounds of molybdenum with the halogens, especially with iodine and fluorine, the authors observed a fact previously noticed by Kestner, viz., that molybdic anhydride, when placed in contact with aqueous hydriodic acid, is reduced to lower oxides, of red colour changing to blue, the reaction being attended with liberation of iodine. With a concentrated solution of hydriodic acid, however, they find that the liquid assumes a deep red colour, and does not contain the lower oxides above mentioned. The same reaction takes place, even in the cold, whenever a molybdate is dissolved in excess of hydrochloric acid and potassium iodide is added, but it requires a certain time and a slight application of heat. Under these circumstances the quantity of iodine set free is always proportional to that of the molybdenum trioxide in the molybdate, and exactly in the ratio of 127:144. The product is a deep red liquid, which when freed from iodine by means of thiosulphate, exhibits a colour similar to that of potassium dichromate, due to a compound which gives with ammonia a precipitate of hydrated molybdenum dioxide, having a rusty colour like that of ferric hydrate. On filtering, a colourless liquid is obtained, in which the presence of molybdenum trioxide may be recognised. This compound, moreover, reacts with ammonia in the same manner as molybdenum pentachloride, a fact which, when viewed in connection with the constant proportionality between the iodine set free and the molybdic anhydride employed, leads to the supposition that the reaction takes place in the manner represented by the equation $2\text{MoO}_3 + 4\text{HI} = \text{I}_2 + \text{Mo}_2\text{O}_4\text{I}_2 + 2\text{H}_2\text{O}$.

On these facts the authors have founded a method of volumetrically

estimating molybdenum in molybdates, which they find to be both rapid and exact. The molybdate (2 to 5 decigrams) is introduced into a glass tube about 2.5 cm. long, 1 cm. in internal diameter, and somewhat enlarged at the bottom, and is dissolved in $2\frac{1}{2}$ c.c. of strong hydrochloric acid of sp. gr. about 1.20. The air having been expelled by a stream of carbonic anhydride, 1.5 gram of potassium iodide dissolved in an equal weight of water is added; the tube, after having been sealed, is left for about an hour and a half in boiling water, opened when quite cold, and the contents, diluted with a large quantity of water, are transferred to a beaker. The iodine is then determined by means of thiosulphate, and the molybdenum trioxide calculated therefrom according to the above-mentioned proportion 127 : 144. Analyses of the molybdates of ammonium, potassium, and sodium-ammonium made in this manner gave very satisfactory results.

Finally the authors have examined the action of molybdenum trioxide in excess on hydriodic acid, by distilling in a retort 0.6198 gram of ammonium molybdate dissolved in excess of hydrochloric acid with 0.2286 gram of potassium iodide. The whole of the iodine is then set free, and there remains a liquid holding in suspension a blue mixed oxide of molybdenum, convertible into the trioxide by the action of permanganate. This reaction may be made available for estimating iodine in iodides, the results being more exact than those obtained with ferric or cupric sulphate.

H. W.

Evaporation of Glycerol. By G. COUTTOLENC (*Bull. Soc. Chim.* [2], **36**, 133—136).—From a series of experiments on the evaporation of anhydrous and aqueous glycerol, it appears that (1) at 90° aqueous glycerol loses its water after heating for five hours on a water-bath. (2.) The amount of evaporation of the glycerol per hour is proportional to the surface exposed, for the same temperature, but by mixing it with sand it is greatly increased. (3.) The evaporation rapidly diminishes with the temperature. (4.) The presence of large quantities of water causes a loss of glycerol, but it is not proportional to the quantity of water added. Glycerol therefore cannot be accurately determined by desiccation at 90°.

L. T. O'S.

New Method of Analysing Oils. By E. J. MAUMENÉ (*Compt. rend.*, **92**, 723).—10 c.c. of oil are heated for an hour in the water-bath with 20 c.c. of a potassium hydroxide solution, which neutralised 123 c.c. of normal sulphuric acid. Various specimens of linseed oil all gave a solid soap, which was separated from the liquid, and the unused alkali estimated. The acid neutralised varied from 105 c.c. to 72.3 c.c. instead of 123 c.c.

C. W. W.

Influence of Frost on Analyses of Sugar Beets. By F. NINGER (*Bied. Centr.*, 1881, 198—199).—This paper draws attention to grave errors which have occurred in the valuation of these roots when examined in a frozen state or but partially thawed. The juices of the root are not equally affected by frost; those portions which contain less sugar become frozen at a higher temperature than the richer portions, and thaw out first, so that if the root is valued in a

partially frozen state, without ample precautions, errors are sure to result.

The author cut some beets in halves; in one half he estimated the sugar immediately, and in the other after thoroughly freezing and thawing. It will be perceived that the total sugar in the latter is higher than the former, which the author accounts for by the increase of volume of the contained water when frozen, forcing a certain quantity to the surface of the root, where it is first thawed and disappears. This amounts to 3 per cent. of the total weight.

	Degrees, Ballg.	Percentage sugar.
Fresh roots.	15.6	12.78
Frozen and thawed roots—		
First pressure	21.7 } average	18.16 } average
Second pressure ..	11.0 } 16.35	8.16 } 13.41

J. F.

Estimation of Tannin in Sumach. By I. MACAGNO (*Gazzetta*, 1881, 297—300).—The author, in estimating the proportion of tannin in Sicilian sumachs by titration with permanganate solution, according to Löwenthal's method (this Journal, 1877, 1, 745) obtained results varying from 21 to 30 per cent., whereas it appears that these same tannins when examined by English analysts, using the old process of Davy—which consists in precipitating the tannin with solution of gelatin, drying the precipitate, and multiplying its weight by 0.4—appeared to yield only 11 to 16, or at most 20 per cent. of tannin. Another process used by English analysts, viz., that of Gerland, consisting in precipitating the tannin with a titrated solution of tartar-emetic, again gives different results, varying from 14 to 20 per cent. The following are the results obtained by the author in applying these different processes to infusions of sumach, and to solutions of pure tannin:—

	Tannin per cent		
	Löwenthal.	Davy.	Gerland.
1. Sumach	21.61	11.10	14.38
2. „	24.93	13.76	16.60
3. „	29.29	15.60	19.54
4. Solution of pure tannin..	20.00	10.68	13.32
5. „ „ ..	30.00	16.00	20.01

The numbers in these three columns are nearly proportional to one another, those obtained by Gerland's process being exactly $1\frac{2}{3}$ of the true quantity of tannin given by that of Löwenthal. In consequence of these differences, the author recommends that in stating the proportion of tannin found in any given tanning material, the process followed by the analyst should in all cases be indicated. H W.

Estimation of Urea by Means of Standard Sodium Hypobromite. By QUINQUAUD (*Compt. rend.*, 93, 82—83).—The sodium hypobromite solution is titrated by means of a centinormal solution of an alkaline arsenite, the indicator used being indigo sulphate, which

gives a greenish-yellow coloration with the alkaline arsenite, disappearing on the addition of the least excess of hypobromite. The intensity of the coloration diminishes gradually as the hypobromite is added, and the indication may be rendered more delicate by adding a fresh drop of indigo solution just before the termination of the reaction. To estimate the amount of urea in a liquid, a slight excess of standard hypobromite solution is added, then a slight excess of alkaline arsenite solution, the excess of the latter being determined by means of the hypobromite. In a series of experiments made with hypobromite solutions containing different proportions of water, sodium hydroxide, and bromine, the author found that the true ratio of 3 mols. hypobromite to 1 mol. urea was only obtained with a hypobromite solution containing 28 c.c. water, 100 c.c. sodium hydroxide solution, and 2.8 to 3 c.c. bromine. With this solution, the whole of the nitrogen was given off.

C. H. B.

Estimation of the Residues of Wines. By L. DE ST. MARTIN (*Bull. Soc. Chim.* [2], **36**, 139—144).—The author defends the old method for the estimation of the residues of wines generally, against the attacks of De la Source and Gautier, and shows that results sufficiently accurate are obtained by the evaporation of 5 c.c. of wine at 100° for 10 hours, without the addition of any foreign body, which, although it assists the desiccation of the wine, increases the evaporation of glycerol, &c. The author considers Gautier's method too tedious for ordinary use, and liable to be influenced by the atmospheric temperature. Moreover the colouring matter of red wines, especially those of recent date, seems obstinately to retain some of the water at the ordinary temperature. The author obtains favourable results by evaporating the wine at 50° in a current of air under reduced pressure.

L. T. O'S.

Technical Chemistry.

Poisoning by Carbonic Oxide. By M. GRUBER (*Dingl. polyt. J.*, **241**, 219—224).—The author confirms the statements made by Fischer (*ibid.*, **235**, 438), Weyl and Fodor (*ibid.*, **237**, 455), and Biefel and Poleck (this Journal, **40**, 853). His experiments were made with a mixture of air and 0.02 to 0.5 per cent. carbonic oxide on rabbits, fowls, and white mice, the time of exposure being spread over a period of ten hours to three days and a half. Poisonous or injurious effects were noticed with very small quantities of the gaseous mixture. The limit of poisoning depends on the concentration of the gas, and not on the time of exposure. Carbonic oxide is inactive when present in the air to the extent of only 0.02 to 0.5 per cent. The following method was found to give approximate results in reference to the hygienic importance of carbonic oxide:—20 litres of air to be examined are shaken up with 10 c.c. of blood, and the

latter tested for carbonic oxide, according to Fodor's method. The washings are examined in the spectrum. If Fodor's reaction is obtained but no reaction in the spectrum, it proves that the percentage of carbonic oxide is less than 0.1 per cent., and more than 0.05 per cent. 100 c.c. of the air to be examined are then treated by Vogel's method. If on examination of the large portion of air (20 liters) absorption-bands are obtained, and the smaller portion does not show anything, the percentage of carbonic oxide varies between 0.1 and 0.25 per cent. Air contaminated with 0.25 per cent. carbonic oxide is highly poisonous. With regard to the presence of coal-gas and carbonic oxide in dwelling rooms, the author mentions that their smell can always be recognised before it is possible to identify their presence. He further remarks that in no case could carbonic oxide be found when rooms were heated with hot air or iron stoves.

D. B.

Relations Between Oxygen and Organic Matter in Various Waters. By T. WEYL and X. ZEITLER (*Bied. Centr.*, 1881, 363—364).—Of the seven samples of water examined, only one was good. The oxygen was determined by Schützenberger's, and the organic matter of Kubel's process. With two exceptions, the quantity of gaseous oxygen varied inversely with the amount of organic matter, but could on no account be taken as a measure of the purity of the water, especially as it varied at different times.

J. K. C.

Manufacture of Potassium Carbonate. By R. ENGEL (*Compt. rend.*, 92, 725).—The aqueous solution of potassium chloride is shaken with magnesia or magnesium carbonate, in presence of carbonic acid. An insoluble crystalline magnesium and potassium carbonate is formed, which separates easily from the mother-liquor. The reaction takes place according to the equation $3\text{MgCO}_3 + 2\text{KCl} + \text{CO}_2 + \text{H}_2\text{O} = 2(\text{MgCO}_3, \text{KHCO}_3) + \text{MgCl}_2$.

When this double salt is heated, either in the dry state or in presence of water, it is decomposed into carbonate of potassium, carbonate of magnesium, carbonic acid, and water. The potassium carbonate may be washed out with water, and dried. The carbonate of magnesium and the carbonic acid may be used for a subsequent operation.

C. W. W.

Magnesia Industry. By T. SCHLOESING (*Compt. rend.*, 93, 156—159, and 215—217).—The author proposes to precipitate the ammonia in sewage in the form of magnesium ammonium phosphate, utilising for the formation of this compound the phosphoric acid also present in the sewage. In order to carry out this process it is necessary to obtain magnesia cheaply, and in a convenient form. For this purpose he proposes the following process:—When dry slaked lime is moistened with magnesium chloride solution, it sets hard, and a fragment of the hardened mass suspended in a solution of magnesium chloride is entirely converted after a time into magnesium hydrate, the lime being removed in the form of calcium chloride. The masses of magnesium hydrate may be washed by diffusion, and when triturated with

water and dried give a compact friable powder. In actual practice, a paste of slaked lime and water containing 34 to 36 per cent. of calcium oxide is allowed to run through perforations in a metallic plate into a solution of magnesium chloride containing from 60 to 95 grams per litre. As soon as the lime-paste touches the magnesium solution it becomes coated with a layer of magnesium hydrate, which acts like a shell, causing it to form long vermicelli-like threads, which are entirely converted into magnesium hydrate in about six days. If the lime-paste is too stiff the conversion is not perfect, if too thin the threads fall together and impede the diffusion of the solution. If the magnesium chloride solution is too strong or too dilute, the magnesium hydrate is too dense or too bulky as the case may be. It is evident that in order to obtain a solution of the required degree of concentration, the mother-liquors from the marine salt works will have to be diluted rather than concentrated. The time of conversion is independent of the strength of the solution within the limits given, and the presence of sodium chloride exercises no effect. Soluble sulphates must be removed, and this may be done by adding the required quantity of calcium chloride solution formed in a previous operation, and allowing the precipitated calcium sulphate to settle.

C. H. B.

Contributions to our Knowledge of Cement. (*Dingl. polyt. J.*, 241, 66—69, 133—138, and 199—204).—Schiffner mentions that when cement is ground by millstones it has only half the firmness which it shows when ground in centrifugal machines. This difference is explained by the fact that centrifugal machines yield a more finely divided product, which, according to Delbrück, increases the hardening power of cement mixed with sand.

Tomei describes a new apparatus for grinding and sifting cement, consisting of a pair of crushing machines, millstones, and sieves with vibrating motion. The latter are made of perforated sheets of steel. This apparatus can be worked with great economy, as the crushing machines break up the coarse pieces, thus preventing the rapid wearing of the stones.

Referring to the artificial modes of drying cement, Bernoulli gives the preference to drying chambers heated with a direct fire, over kilns fed with a coke fire. With regard to the burning of cement, it is mentioned that annular kilns are at present mostly used, although the ordinary pit-furnaces are still in existence to a large extent; the heat which is lost in these kilns is utilised for drying purposes. Tomei has constructed a circular furnace, consisting of twelve ordinary pit furnaces, the flues of which are built round a shaft. The saving in fuel is said to be equal to 30 per cent., as compared with the consumption in pit furnaces.

Goslich has investigated the action of the addition of fine sand and other finely ground substances on the solidity of cement, and found that coarse sand gives the highest numbers for firmness. Experiments have shown that in order to increase the solidity of cement, when coarse sand of one sized grain is used, it is unnecessary to mix fine sand

with it, so as to fill up the hollow spaces, as other indifferent substances can be used with equally good results.

Tomei has made a series of experiments to ascertain the influence which the air has on cement. He concludes that carbonic anhydride *per se* is injurious only when present in great excess. However, moist carbonic anhydride, as it is found in practice, decreases the firmness of cement to a considerable degree, and in a short space of time.

Froiderville mentions that the great difficulty in manufacturing marble-imitations from cement is to prevent the cracking of the latter. Cement cracks when it is made up with too much water, it then forms a vitreous crust, and is not homogeneous through the entire mass. By adding granite to cement without sand, a material of great hardness is obtained, which can be polished. D. B.

Adulteration of Cane-sugar with Glucose. By P. CASAMAJOR and others (*Bied. Centr.*, 1881, 206—207).—The adulteration of cane-sugars and syrups has been carried to a large extent in the United States, the light colour of glucose giving a false appearance of superior quality at the expense of its sweetening properties.

Casamajor, besides detecting the adulteration in the usual optical manner, and by reduction of Fehling's solution, suggests a method by which consumers ignorant of chemistry may examine the suspected sugar, a portion of which being dissolved in a flat beaker with somewhat less than its own weight of water, the cane-sugar either dissolves completely or becomes transparent, whilst the glucose floats as white flocculent particles like flour. Drummond says that when coffee is sweetened with adulterated sugar, a deposit forms in the bottom of the vessel which, when dried, becomes gelatinous, hardens, and presents peculiar appearances under the microscope.

Casamajor recommends as a second test the dissolving of a small quantity of pure sugar on the tongue, and when the mouth is fully engaged with the pure flavour, a small quantity of the suspected sample is introduced; if glucose be present, a bitter taste will be distinctly perceptible. Another method recommended is to saturate methyl alcohol with glucose, and to digest the sample therein; the cane-sugar is dissolved and glucose if present remains, the alcohol being unable to take it up. J. F.

Analyses of Beet-molasses. By H. BODENBENDER and others (*Bied. Centr.*, 1881, 409—413).—Slaked lime will do just as well as quicklime for the precipitation of lime-sugar from molasses. As the mean result of sixteen analyses, the following amounts of nitrogen and nitrogenous bodies were found in 100 parts of molasses. Total nitrogen, 1.5051; nitrogen as ammonia salts, 0.0383; in the form of amides (asparagine and glutamine), 0.0246; as amido-acids (aspartic and glutamic), 0.4583; and as betain and protein, 0.9839. In the estimation of these bodies Sachsse's method was used. The total percentage of nitrogenous bodies was found to be 11.53.

J. K. C.

Disadvantages of Cooling-pans in Distilleries. By P. WITTELSHÖFER (*Bied. Centr.*, 1881, 417—418).—When the mash is left to

cool in pans in the air during the hot season, a considerable loss of alcohol occurs, partly from evaporation, and partly from the injurious effects of the lactic acid formed in the mash during the lengthy process of air-cooling. The author, therefore, recommends that artificial refrigeration be resorted to whenever possible.

J. K. C.

Fermentation of Italian Wines. By NESSLER (*Bied. Centr.*, 1881, 428).—The fermentation of must from Italian grapes is often a difficult process, the yeast separating from the liquor before the fermentation is complete. As the quality of the wine depends to a great extent on the success of the fermentation, great care has to be taken with the must, which differs in this respect from the must of German grapes.

J. K. C.

Influence of Acids on the Preservation of Wine. By E. MACH and K. PORTELE (*Bied. Centr.*, 1881, 483).—Organic acids, as tartaric acid, tannic, &c., greatly aid in the preservation of wine, preventing or reducing the formation of fungi. Succinic acid has, however, but little influence.

E. W. P.

Analyses of Wine and Must. By J. MORITZ (*Bied. Centr.*, 1881, 417).—From the relation of the quantities of acid and sugar in a wine, the author obtains a number which he considers as a measure of the quality of the wine.

J. K. C.

Interference of Bacteria with Brewing. By MARPMANN (*Bied. Centr.*, 1881, 431—432).—A peculiar after-fermentation set in in a brewery, which had never been observed before. The beer became sour and putrid, and the air surrounding the vats was found to be full of bacteria. The place was disinfected with burning wood and carbolic acid, and the fermentation then proceeded as usual.

J. K. C.

Influence of Malt on the Quality and Keeping Properties of Beer. By LINTNER (*Bied. Centr.*, 1881, 204—206).—The author attributes many of the complaints of muddy beer, now prevalent in Germany, to the employment of an insufficient quantity of yeast, and allowing the fermentation to proceed at too low a temperature, and concludes, that when a sufficient quantity of yeast is employed, the development of the cells and commencement of fermentation go on simultaneously; whilst in cases where a deficiency exists, a part of the cells are growing, and another part have started fermentation, so that the process is irregular, and protein substances which, under ordinary circumstances, should have been used up by the yeast are left: and, on the contrary, when a larger quantity than is necessary is used, it does not act hurtfully, but prevents the growth of other organisms which tend to render the beer thick.

J. F.

General and Physical Chemistry.

Telluric Rays of the Solar Spectrum. By N. E. GOROFF (*Compt. rend.*, 93, 385—387).—The author draws attention to the incompleteness of former researches on the telluric rays in the following points:—1st. The observation of the extreme red ($A-\alpha$) of the absorption spectrum of water. 2nd. The order of appearance of the absorption bands of water-vapour in proportion to the increase of thickness of the absorbing layer and its density.

Ångström has observed on very cold days the disappearance of all the telluric lines with the exception of A, part of B, C_δ , or α and δ , which he attributes to carbonic anhydride or ozone, but without supporting his supposition by experiment. The author's researches lead him to believe that the absorption spectrum of water is the only one remaining at low pressures. By passing the rays of a powerful electric light through a layer of vapour of water 18 meters thick, and gradually increasing its tension to 6 atmospheres, the following changes were observed:—At 6—3 atmospheres all absorption groups, after α , observed by Janssen, were visible; at 4 atmospheres the lines at the yellow border of D became indistinct; at 3—2.5 atmospheres the C and D groups and the orange border of D were indistinct; at 2 atmospheres only A and B were perceived; and at 1.5—1 atmosphere only α remained. Hence it appears that α is the fundamental group for water vapour and during summer a layer of atmospheric air 500 meters thick would be sufficient to produce it. These results agree with those of Crocé Spinetti and Piazzzi Smyth. It was also found by observations in the depth of winter, that the absorption spectrum of the atmosphere was perfectly free from the groups α and B, which are characteristic of the vapour of water, only a part of the band B, neighbouring bands of D, and what seemed to be δ , were visible. The author proposes to carry on researches in the winter with a view of deciding the question of the presence and variation of ozone and the oxides of nitrogen in the atmosphere.

V. H. V.

Absorption of the Ultra-violet Rays. By DE CHARDONNET (*Compt. rend.*, 93, 406—409).—The author adopted two methods for the examination of the absorptive power of ultra-violet rays by liquids. In the one method the solar rays were passed through a column of the liquid from 3—20 mm., enclosed in a tube fitted at each end with quartz plates; the luminous rays were then thrown on photochromic paper, whose change of tint indicated the presence or absence of chemical rays. In the second method, the solar rays reflected from a heliostat, after passing through a narrow slit, were decomposed by an Iceland spar prism, and the spectrum projected on to a photographic plate or a fluorescent screen. A vessel of quartz, partially filled with the liquid to be tested, was then interposed in front of the slit so as to project on the screen the solar and the absorption spectra in juxtaposition. By this apparatus, the author

examined various extracts from vegetables, and found that they all exert a most marked absorptive power on actinic rays; liquids of animal origin were also examined with various results. Distilled water, alcohol, ether, &c., have no action, but gelatin absorbs all the actinic rays from the ray G, and is fluorescent in all parts of the actinic spectrum.

V. H. V.

A Curious Actinic Phenomenon. By T. L. PHIPSON (*Chem. News*, **44**, 73; see this vol., 863).—The darkening of the zinc pigment is due to reduction, and the return to whiteness in the dark is accompanied by a process of oxidation. Pyrogallol facilitates the reduction and causes it to take place to some extent under glass. The dark product is soluble in acetic acid, and from this solution, after neutralisation, ammonium sulphide throws down a dark green precipitate which becomes white on oxidation, and contains zinc and iron. Previous to the action of light, acetic acid does not dissolve out the substance to which the phenomenon is due. The darkening is not caused by the presence of minute traces of iron, but may be due to the presence of a new metal associated with the zinc (see p. 1104).

C. H. B.

Improvements in Batteries. By D. LINDO (*Chem. News*, **44**, 77).—Azapis has recommended the substitution of a solution of sodium or ammonium chloride for the dilute acid in a Bunsen cell. The author finds this to be a great improvement. The zinc need not be amalgamated. A solution of 1 part sodium sulphate in 5 parts water may with equal advantage be substituted for the dilute sulphuric acid in both Groves and Bunsen's cells.

C. H. B.

The Circuit Produced by the Reaction Current of Electrolysis and by Evaporation and Condensation. By J. MOSER (*Ann. Phys. Chem.* [2], **14**, 62—84).—In the first part of the paper the author deals with the phenomenon of a galvanic element, in which the motive power is the attraction between water and a dissolved salt, the influence of all ordinary chemical affinities being avoided. For this purpose the parts of the element merely differ in degree of concentration, whilst the electrodes in all cases consist of the same metal as that of the dissolved salt. Two vessels containing solutions of the same salt, of different degrees of concentration, are connected by a syphon and placed in the galvanic circuit by means of electrodes of the same metal as that of the dissolved salt. With this arrangement it was found that in all cases (sulphates, chlorides, nitrates, acetates, &c., of zinc, copper, iron, silver, &c.) an electromotive power is produced which acts in a direction opposite to that of the electrolytic battery, and that the attraction between the salt and the water goes from the more dilute to the more concentrated solution. The second part of the paper gives the mathematical development of the theory of the reaction current produced by evaporation and condensation.

T. C.

Specific Heat and Heat of Dilution of Perchloric Acid. By BERTHELOT (*Compt. rend.*, **93**, 291—292).—The molecular specific

heats of solutions of perchloric acid (between 40° and 15°) can be represented by the following empirical formula which obtains up to $n = 3$ for solutions $\text{HClO}_4 + n\text{H}_2\text{O}$:—

$$C = 18n - 2.3 + \frac{273.8}{n} - \frac{742.2}{n}$$

In the table below the experimental results are given.

Composition $\text{HClO}_4 +$	Specific heat for unit weight.	Molecular heat $n\text{H}_2\text{O} +$
3.08 H_2O	0.501	11.31
5.4 H_2O	0.575	8.5
9.59 H_2O	0.6705	5.25
46.35 H_2O	0.893	0.3
590 H_2O	0.993	—

The heats of dilution of acids of various strengths were measured, and from the results it was found that the heat disengaged can be represented by a curve of the hyperbola form; starting from the most concentrated acid to $n = 2$, the curve is identical with its tangent; then from $n = 3$ to $n = 9.5$ the curve bends rapidly, and in this portion of the curve, whilst the quantities of added water increase in arithmetical proportion, the quantities of heat disengaged decrease in geometrical proportion, and finally the curve cuts the axis x for $n = 9.85$. This curve of hydration of perchloric acid is similar to the curves of hydration of nitric acid and sodium hydroxide.

V. H. V.

Heat of Formation of Potassium Perchlorate. By BERTHELOT and VIEILLE (*Compt. rend.*, 93, 289—291).—The authors have determined the heat of formation of potassium perchlorate, by mixing it with an exact equivalent of an explosive substance, such as potassium or ammonium picrate, which is capable of reacting instantaneously with the salt. These same substances were burnt with free oxygen, and the difference between the two quantities of heat evolved in the two reactions represents the excess of heat developed by the action of free oxygen over the heat developed by the action of the combined oxygen, that is to say (the heat absorbed or evolved) by the decomposition of potassium perchlorate into potassium chloride and oxygen. The authors found as a mean of the actions of potassium and ammonium picrate the value -7.5 cal. for the reaction, KClO_4 (solid) = KCl (solid) + 2O_2 , whereas the analogous decomposition of potassium chlorate evolves + 11.0 cal. From this determination, the heat of formation of potassium perchlorate can be ascertained; according to Thomsen's experiments—

$\text{K} + \text{Cl} = \text{KCl}$ (solid) disengages + 105 cal.
hence—

$\text{K} + \text{Cl} + 2\text{O}_2 = \text{KClO}_4$ (solid) disengages + 112.5 cal.

V. H. V.

Vapour-tension of Mixed Liquids. By D. KONOVALOFF (*Ann. Phys. Chem.* [2], 14, 34—52).—The author has investigated this subject with respect to the first four alcohols of the series $\text{C}_n\text{H}_{2n+2}\text{O}$, and

the first four acids of the series $C_nH_{2n}O_2$, when mixed with water, and from the results obtained the following conclusion is drawn:—*Every mixture which exhibits a maximum or minimum vapour-tension, has at the corresponding temperature the same composition as its vapour.* Consequently all mixtures of liquids are divisible into three distinct groups, according to their behaviour on distillation.

1. Those whose vapour-tension curve shows neither a maximum nor a minimum, and which, therefore, have never the same composition as their vapour whatever the proportions in which they are mixed, the composition varying continually as the distillation proceeds. Such mixtures never exhibit a constant boiling point.

2. Mixtures whose vapour-tension curve shows a maximum. On evaporation at a constant temperature, a residue is obtained, the vapour-tension and composition of which is removed from that of the maximum, whilst the first-formed vapour is near the maximum; on distillation under constant pressure, the composition of the residue is very different from that corresponding to the minimum boiling temperature, whereas the first distillate approximates to it. It consequently follows that on distilling repeatedly the first portion which comes over, a distillate is finally obtained, having a minimum and constant boiling point. And secondly, on further distillation of the rest of the mixture, a residue is left, which contains only one of the liquids, but which this is depends on the composition of the original mixture. Propyl alcohol and butyric acid belong to this group, the former giving a liquid of constant boiling point, when mixed with 77 per cent. of water; and the latter a constant boiling point of 99.5° when mixed with 75 per cent. of water.

3. Those mixtures whose tension curve shows a minimum. These, on continued distillation of the residue, finally give a liquid of minimum tension; whilst the final distillate, obtained by the repeated distillation of the first portion which comes over, consists solely of that constituent which lies on the same side of the minimum as the original mixture. Formic acid belongs to this class, boiling constantly when mixed with 22.5 per cent. water at 107.1° , as already shown by Roscoe (*Annalen*, **112**, 327; **116**, 203).

In the case of all mixtures of constant boiling point, the latter is either *higher or lower than that of each constituent, i.e.*, their tension curves exhibit either a minimum or a maximum. T. C.

Compressibility of Carbonic Anhydride and of Air under Low Pressures and at High Temperatures. By E. H. AMAGAT (*Compt. rend.*, **93**, 306—308).—A continuation of the author's researches (see this vol., p. 12). The study of the compressibility of gases under low pressure and at high temperatures, presents certain difficulties which arise from the necessary correction for the tension of the vapour of mercury; but, even if this correction is made, it is scarcely probable that the mercurial vapour forms an atmosphere of constant density from the surface of the meniscus to the end of the manometer tube. Regnault has shown that at 300° the tension of vapour of mercury is 0.24 m., so the error arising from so large a correction, when experiments are made only under a few meters pres-

sure, renders the results practically valueless. The author has repeated his former experiments on the compressibility of gases (*Ann. Chim. Phys.* [4], 29) with an improved apparatus, and more accurate methods of working, and has studied carbonic anhydride and air.

Air follows Mariotte's law regularly from 100—300°, under pressures between 1 and 8 atmospheres, within which limits the values of $\frac{pv}{p'v'}$ ($v = 2v'$) do not sensibly vary; the results of various series at 100° lay between the numbers 1·0008 and 0·9985, and at 300° between 1·0005 and 0·997.

In the following table are given the corresponding results obtained with carbonic anhydride:—

Initial pressure in atmospheres.	Values of $\frac{pv}{p'v'}$ ($v = 2v'$).			
	Temp. 50°.	100°.	200°.	300°.
0·725	1·0037	1·0021	1·0009	1·0003
1·440	1·0075	1·0048	1·0025	1·0015
2·850	1·0145	1·0087	1·0040	1·0020

These show that the variations of carbonic anhydride at 50° and at 100° are very appreciable, and that they increase proportionately to the initial pressure; the results at 200° also lead to the same conclusion. At 300° the variations between 1 and 2 atmospheres are *nil*, but they increase slightly between 2 and 4 atmospheres. The results are in accordance with those obtained by the author in his former researches on other gases.

V. H. V.

Dissociation: Comparison of Formulæ deduced from Experiment. By G. LEMOINE (*Compt. rend.*, 93, 312—315).—The author illustrates by experimental data the theory of dissociation proposed for gaseous homogeneous systems at sufficiently low pressures (*Compt. rend.*, 93, 265). This theory is expressed in the following formula, in which p is the number of molecules of the compound possible in a volume of 1 litre, γ the number of molecules of the compounds dissociated, μ the number of equivalents in excess of one of the elements, a , b , and β constants.

$$\frac{d\gamma}{dt} = a \left(1 - \frac{\gamma}{p}\right) - b \left(\frac{\gamma}{p}\right)^{2\beta} p^{2\beta-1} \left[1 + \left(\frac{\mu}{\gamma}\right)\right]^{\beta}$$

Hydriodic Acid (*Compt. rend.*, 1875, 1877).—The influence of pressure on the limit of dissociation, at a temperature of 440°, depends entirely on the constant β . It is found on calculation that $\beta = 0·553$, and that this value gives satisfactory results for intermediate pressures.

The influence of the excess of one of the dissociated bodies at a temperature of 440° can be calculated by means of this value for β ; the results, however, vary but little, even with considerable variations of β . In the following table the experimental and theoretical results are compared:—

Composition in equivalents.	Ratio of free to total hydrogen.		
	Experiment.	Theory $\beta = 0.553.$	Theory $\beta = 1.$
H + I	0.24	0.24	0.24
H + 0.784 I	0.350	0.344	0.354
H + 0.527 I	0.547	0.521	0.535
H + 0.258 I	0.774	0.753	0.765

Combination of Dimethyl Ether with Hydrochloric Acid (Friedel, *Bull. Soc. Chim.*, 1875).—The influence of pressure on the limit of dissociation can be studied, as in the case of hydriodic acid ($\beta = 1.22$ or 1.13, approximately 1).

Pressure in atmospheres.	Fraction of dissociation $\frac{\gamma}{p}$.		
	Experiment.	Theory $\beta = 1.22.$	Theory with $\beta 1.00.$
0.882	0.876	0.876	0.876
1.118	0.843	0.839	0.850
1.447	0.790	0.790	0.817
3.000	—	0.618	0.702
5.000	—	0.490	0.607

Curves are given illustrating the experimental results tabulated above.

Polymeric Transformation of Iodine Vapour (Crafts and Meier, *Abstr.*, 1880, 788, 433).—The same formula can be applied as in the two cases above.

Pressure in atmospheres at 1250°.	Observed density.	Calculated density $\beta = 1.$
1.0	5.89	6.21
0.4	5.54	5.54
0.3	5.30	5.35
0.2	5.07	5.12
0.1	4.72	4.82

Calcium and Barium Bicarbonates (Schlœsing, *Compt. rend.*, 1872).—In a litre of water, supposing there is a constant weight p of calcium carbonate in solution, and the exterior atmosphere of carbonic anhydride at such a tension that a litre dissolves a weight x of the gas, so that a weight γ of the bicarbonate will exist in any given instant,—the surrounding heat tends to destroy the bicarbonate, and the weight decomposed in the time determined is proportional to the mass γ ; but there is formed at the same time a quantity of the bicarbonate, dependent on the masses p and x of the neutral carbonate and carbonic anhydride, and proportional to $p^\beta x^\beta$. Then k' and k being constant, the equation of dissociation is—

$$k'\gamma = kp^\beta x^\beta,$$

or uniting the constants k' , k , and p^β into a single constant k , the equation becomes—

$$x^\beta = k\gamma,$$

which is the equation given by Schlœsing.

V. H. V.

Inorganic Chemistry.

Explosion in preparing Oxygen. By S. LIMOUSIN (*Chem. Centr.*, 1881, 76—77).—In preparing oxygen from potassium chlorate alone in a retort of 80—90 litres capacity, a violent explosion occurred in the gasometer.

The author considers this due to some hydrocarbons evolved from a caoutchouc tube connecting the retort with the wash-bottle forming an explosive mixture in the gasometer with the oxygen. F. L. T.

Action of Sulphur on Certain Metallic Solutions. By E. FILHOL and SENDERENS (*Compt. rend.*, 93, 152—154).—Finely divided sulphur decomposes boiling aqueous solutions of silver sulphate, nitrate, carbonate, oxalate, and acetate, with formation of silver sulphide, and, in some cases, free sulphuric acid, the acid combined with the silver being set free. Silver chloride, under the same conditions, is not decomposed. These results are in accordance with thermochemical data. Lead sulphate is very slowly decomposed by sulphur, and the supernatant liquid is not acid, probably owing to the formation of lead bisulphate. Copper sulphate, nitrate, and chloride are not decomposed. C. H. B.

Amount of Sulphuric Anhydride in Fuming Sulphuric Acid. By C. WINKLER (*Chem. Centr.*, 1881, 44—45).—The author weighs out a portion of the acid, dissolves it in water, and titrates with normal potassium hydroxide, the acid being poured into the water in a thin stream. When the fuming acid is solid, it must first be melted. It is not essential that the sample be fully molten, as the composition of the solid and liquid portions are shown to be practically identical. The solid acid must not be poured directly into water, as loss would occur, but must first be diluted with an acid of known strength. The amount of sulphurous acid was determined, after solution in water, by permanganate. The following table gives the composition of acids of different densities, the solid acids being fused before determination:—

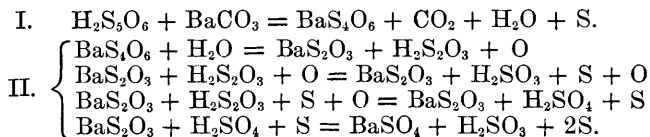
Sp. gr. at 20°.	Per cent. of		Per cent. of		Per cent. of		
	SO ₃ .	H ₂ O.	SO ₃ .	Sulphuric acid of 66° B.	SO ₃ , volatile on heating.	Monohy- drate, H ₂ SO ₄ .	Water.
1·835	75·31	24·69	—	100·00	—	92·25	7·75
1·840	77·38	22·62	8·39	91·61	—	94·79	5·21
1·845	79·28	20·72	16·08	83·92	—	97·11	2·89
1·850	80·01	19·99	19·04	80·96	—	98·01	1·99
1·855	80·95	19·05	22·85	77·15	—	99·16	0·84
1·860	81·84	18·16	26·45	73·55	1·54	98·46	—
1·865	82·12	17·88	27·57	72·43	2·66	97·34	—
1·870	82·41	17·59	28·76	71·24	4·28	95·76	—

Sp. gr. at 20°.	Per cent. of		Per cent. of		Per cent. of		
	SO ₃ .	H ₂ O.	SO ₃ .	Sulphuric acid of 66° B.	SO ₃ , volatile on heating.	Monohy- drate, H ₂ SO ₄ .	Water.
1·875	82·63	17·37	29·95	70·05	5·44	94·56	—
1·880	82·81	17·19	30·38	69·62	6·42	93·58	—
1·885	82·97	17·03	31·03	68·97	7·29	92·71	—
1·890	83·13	16·87	31·67	68·33	8·16	91·84	—
1·895	83·43	16·66	32·52	67·48	9·34	90·66	—
1·900	83·48	16·52	33·09	66·91	10·07	89·93	—
1·905	83·57	16·43	33·46	66·54	10·56	89·44	—
1·910	83·73	16·27	34·10	65·91	11·43	88·57	—
1·915	84·08	15·92	35·52	64·48	13·33	86·67	—
1·920	84·56	15·44	37·27	62·73	15·95	84·05	—
1·925	85·06	14·94	39·49	60·51	18·67	81·33	—
1·930	85·57	14·43	41·56	58·44	21·34	78·66	—
1·935	86·23	13·77	44·23	55·77	25·65	74·35	—
1·940	86·78	13·22	46·46	53·54	28·03	71·97	—
1·945	87·13	12·87	47·88	52·12	29·94	70·06	—
1·950	87·41	12·59	49·01	50·99	31·46	68·54	—
1·955	87·65	12·35	49·98	50·02	32·77	67·23	—
1·960	88·22	11·78	52·29	47·71	35·87	64·13	—
1·965	88·92	11·08	55·13	44·87	39·68	60·32	—
1·970	89·83	10·17	58·81	41·19	44·64	55·36	—

F. L. T.

Contribution to the Knowledge of the Polythionic Acids contained in Wackenroder's Solution. By T. CURTIUS (*J. pr. Chem.* [2], 24, 225—239).—The author's investigations on the reaction which occurs when Wackenroder's solution is neutralised by a base, agree in part only with the results obtained by Takamatsu and Smith (this Journal, Trans., 1880, 592), by V. Lewes (this Journal, Trans., 1881, 68), and by Stingl and Morawski, and many others. The object of the research was to ascertain what the products are which are formed by the addition of barium carbonate to Wackenroder's solution. This solution was therefore neutralised with barium carbonate, without previous removal of the sulphur formed during its preparation. The neutral solution thus obtained was filtered, and a known volume was mixed with potassium hydroxide solution, and chlorine passed in; all sulphur being thereby oxidised to sulphuric acid, the solution was decomposed with hydrochloric acid, and evaporated. The precipitated barium sulphate was filtered off, and in the filtrate the remaining sulphuric acid was separated by barium chloride. By this method, the ratio between the combined and the uncombined sulphur was determined, and this was found to be 1 : 3; therefore, in the original neutral solution the ratio of barium to sulphur was 1 : 4. The conclusion drawn is, that pentathionic acid, neutralised by barium carbonate, is converted into barium tetrathionate, with separation of sulphur. If the neutralised solution is allowed to remain for some time, it slowly deposits a precipitate,

which, when removed, is soon followed by another precipitate, but of a different composition, and so on. These changes are accelerated by heat, and the precipitates consist of sulphur, thiosulphates, sulphites, and sulphates, the final product being sulphur, sulphites, and sulphates. This is according to the following equations:—



The solution of barium tetrathionate cannot therefore be preserved unaltered, neither are tetrathionates separated on the addition of alcohol; it appears, therefore, that the salt thus prepared is not identical with that prepared by other processes. According to Spring, the addition of alcohol to the solution of barium tetrathionate causes the formation of a precipitate which is not wholly soluble in water. This insoluble portion appears to be barium thiosulphate, or at any rate a mixture having approximately that composition, sulphur being present only in traces. The soluble portion consists of pure barium thiosulphate. It was found impossible to prepare any pure neutral tetrathionates, so recourse was had to the acid salts, which were obtained by evaporating a neutralised Wackenroder's solution with as much of free acid. Lewes obtained salts by concentrating in a vacuum Wackenroder's solution half neutralised with baryta-water or potassium hydroxide; but he obtained a mixture of tetra- and penta-thionates, and finally pentathionate, and the potassium salt was of variable composition. The author succeeded in obtaining well-formed salts, by evaporating down the half-neutralised solution, with carbonates of the weak bases, such as zinc, and filtering off the sulphur and excess of carbonate. By this means, an acid liquid is produced, which, when heated in small quantities in a test-tube, explodes, yielding sulphur, zinc sulphide, sulphurous acid, and sulphuretted hydrogen; if, however, the solution is slowly evaporated at a low temperature, the whole solidifies on cooling to a crystalline mass, consisting of non-deliquescent crystals. The zinc salt is soluble in water; the didymium compound forms hard sandy transparent rose-coloured crystals, of acid reaction, soluble in water, but precipitated from its solution as a red powder by alcohol. The manganese salt is pale red, soluble in water, and deliquescent. All the salts can be preserved unaltered, but at 100° sulphur is separated, as also sulphurous acid and sulphuretted hydrogen. Lewes' compounds, when decomposed, do not produce sulphuretted hydrogen, and therefore they cannot be identical with those obtained by the author.

E. W. P.

New Selenium Compounds. By C. A. CAMERON and E. W. DAVY (*Chem. News*, **44**, 63—64).—*Mercuric selenate*, HgSeO_4 , a white crystalline salt, obtained by the action of selenic acid on mercuric oxide or mercuric acetate. It dissolves in selenic, sulphuric, nitric, and hydrochloric acids, but is decomposed by water, with formation of a basic salt and liberation of selenic acid.

Basic mercuric selenate, $\text{HgSeO}_4(\text{HgO})_2$, prepared by the action of water on the neutral salt, or by addition of selenic acid or a solution of a selenate to a solution of mercuric acetate, is a red compound, soluble in selenic, sulphuric, nitric, and hydrochloric acids, but only sparingly soluble in water. The acid mercuric selenate does not appear to exist.

Mercurous selenate, Hg_2SeO_4 , is a greyish-white amorphous substance, obtained by adding selenic acid or an alkaline selenate to mercurous nitrate. It very rapidly darkens when exposed even to diffused daylight, is insoluble in hydrochloric acid, and but slightly soluble in water. Nitric acid converts it into mercuric selenate, with evolution of nitric oxide.

Dimercurammonium selenate, $(\text{NH}_4)_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$, obtained by treating neutral mercuric selenate, or the freshly prepared basic selenate, with strong ammonia and diluting the solution, is a white compound, which darkens when exposed to light, and dissolves in hydrochloric acid or strong ammonia. When heated, it is decomposed.

When selenic acid is heated with an excess of metallic mercury, a selenite and not a selenate is produced, thus: $\text{Hg} + \text{H}_2\text{SeO}_4 = \text{HgSeO}_3 + \text{H}_2\text{O}$. When, on the other hand, the selenic acid is in excess, the selenite is decomposed, and a selenate is formed. The product usually consists of a mixture of the two salts. The authors were unable to obtain an acid mercuric selenite.

Mercuric selenocyanate, $\text{Hg}(\text{CySe})_2$, is obtained as a white felt-like mass by adding potassium selenocyanate to mercuric acetate. It dissolves freely in solutions of alkaline cyanides, thiocyanates and selenocyanates, and mercuric chloride, with which it forms double salts. It darkens when exposed to light, decomposes at 100° , and when strongly heated, burns in the same remarkable way as the thiocyanate.

Mercurous seleno-cyanate, $\text{Hg}_2(\text{CySe})_2$, an olive-green compound, which decomposes at 100° , is obtained by adding a solution of an alkaline selenocyanate to one of mercurous nitrate.

Ammonium selenocyanate, NH_4CySe , described by Crookes, may be obtained by digesting a mixture of potassium selenocyanate and ammonium sulphate in alcohol. Attempts to form selenurea gave unsatisfactory results.

Potassium selenocyanate and Mercuric cyanide, $\text{KCySe} + \text{HgCy}_2$, is obtained in long prismatic crystals, unaltered by exposure to the air, by adding a strong solution of mercuric cyanide to an aqueous, or better, an alcoholic solution of potassium selenocyanate. It is only slightly soluble in cold water and still less in alcohol, but dissolves in both liquids when heated; sparingly soluble in ether. When it is heated with dilute hydrochloric acid, hydrocyanic acid is given off and selenium separates out.

Potassium selenocyanate and mercuric thiocyanate, $\text{KCySe} + \text{Hg}(\text{CyS})_2$, obtained when an aqueous solution of potassium selenocyanate is heated with mercuric thiocyanate, forms long prismatic colourless crystals, permanent in the air, somewhat soluble in boiling water and alcohol, and slightly soluble in boiling ether. The compound gives the thiocyanate reaction with ferric chloride, and when

heated with hydrochloric acid, is decomposed with separation of selenium and evolution of hydrocyanic acid.

Potassiomericuric selenocyanate, $\text{KCySe}, \text{Hg}(\text{CySe})_2$, is obtained in long six-sided prismatic crystals by dissolving mercuric selenocyanate in a hot solution of potassium selenocyanate, and leaving the liquid to cool. It is readily soluble in water and hot alcohol, but dissolves only to a slight extent in cold alcohol. This salt was not analysed quantitatively.

Potassium selenocyanate and Mercuric iodide, $\text{KCySe} + \text{HgI}_2$, a white crystalline salt, obtained by dissolving mercuric iodide in an aqueous or alcoholic solution of potassium selenocyanate, and leaving the liquid to cool. It is only slightly soluble in cold water and alcohol, but dissolves readily in these liquids when heated. When it is treated with hydrochloric acid, mercuric iodide is at first separated, but this dissolves in excess of acid, giving a colourless solution, which gives off hydrocyanic acid, and deposits selenium when heated. The corresponding mercurous compound could not be obtained. When mercurous iodide is treated with potassium selenocyanate, metallic mercury is separated, and the double mercuric compound formed.

Potassium selenocyanate and Mercuric chloride, $\text{KCySe} + \text{HgCl}_2$, is obtained as a white crystalline salt, by adding an aqueous solution of mercuric chloride drop by drop to an aqueous or alcoholic solution of potassium selenocyanate, until the precipitate at first formed is no longer re-dissolved. When, as in Crookes's experiments, an excess of mercuric chloride is added, a yellow compound of mercuric selenocyanate and chloride is produced. The corresponding bromine compound may be prepared in a similar manner. It forms long flat prismatic crystals. Both compounds dissolve in hot alcohol and water, but are only slightly soluble in these liquids when cold.

All the above compounds may be obtained by boiling selenium with the proper proportion of potassium cyanide in aqueous solution, adding the mercuric salt, filtering whilst hot, and leaving the liquid to cool.

C. H. B.

A New Series of Phosphates and Arsenates. By E. FILHOL and SENDERENS (*Compt. rend.*, **93**, 388).—Berthelot and Louguinine have observed, that in order to attain a solution neutral to colour tests, 1.5 equivalents of sodium hydroxide must be added to one equivalent of phosphoric acid. The authors have obtained from such a solution a sesquisodic phosphate $(\text{P}_2\text{O}_5)_2 \cdot 3\text{NaOH} + \text{H}_2\text{O}$ separating out from a thick viscid liquid, like honey; it is very soluble and slightly deliquescent. An analogous sesquisodic arsenate was obtained, resembling the phosphate in appearance.

V. H. V.

Solubility of Silver in Presence of Iodides. By A. DITTE (*Compt. rend.*, **93**, 415—418).—It has recently been shown by Berthelot that metals which are not altered by the oxygen of the air are readily oxidised when some compound is introduced which unites with evolution of heat with the oxide of the metal (this vol., p. 791). Thus silver, which is not attacked at ordinary temperatures by dry or moist oxygen, if introduced into a 5 : 100 solution of potassium iodide, becomes

covered after a short time with fine crystals of silver iodide; and in a more concentrated solution is converted into a friable mass of the iodide. This reaction is easily accounted for by thermochemical considerations; from the combination of oxygen with silver, 7.0 cal. are evolved, but the reaction, Ag_2O (solid) + 2KI (dissolved) = 2KHO (dissolved) + 2AgI evolves 36.8 cal. Oxygen is absorbed by the silver in contact with the potassium iodide, and that this is really the case is shown by the fact that if the metal is only partly immersed, the formation of the silver iodide is more marked at the point of contact of the metal and liquid. Or, again, if a plate of silver is introduced into a solution of potassium iodide from which the air has previously been removed by boiling, and the solution is kept in a sealed flask, the metal remains unaltered. Although the free potassium hydroxide liberated in the above reaction absorbs carbonic anhydride from the air, and the liquid is always slightly alkaline, yet this in no way influences the result, for potassium carbonate will not decompose silver iodide. If the potassium iodide solution be too concentrated, the silver iodide will dissolve as a double compound of the iodides of potassium and silver, $2(\text{AgIKI})\cdot\text{H}_2\text{O}$, but on adding water, the silver iodide is precipitated. With sodium iodide, the reaction is more marked than with the potassium salt. Deville has shown that silver decomposes potassium iodide melted in a porcelain crucible; the potassium is oxidised and combines with the silica of the porcelain, even reducing it to silicon, but if there is free access of air within the crucible, the silver is attacked and converted into the iodide. Analogous reactions take place in the case of mercury, but gold is unattacked by potassium iodide in a state of fusion in contact with the oxygen of the air.

V. H. V.

Solubility of Magnesium Carbonate in Water Charged with Carbonic Acid. By M. ENGEL and J. VILLE (*Compt. rend.*, 93, 340—341).—The authors allude to the discordant results obtained by former experimenters; they have determined the solubility of magnesium carbonate in water charged with carbonic acid, first, as a function of the pressure, secondly, as a function of the temperature. The results are given in the tables below:—

Pressure in atmospheres.	Temperature.	Quantity of magnesium carbonate dissolved by a litre of water.
1.0	19.5	25.79 grams.
2.1	19.5	33.11 "
3.2	19.7	37.3 "
4.7	19.0	43.5 "
5.6	19.2	46.2 "
6.2	19.2	48.51 "
7.5	19.5	51.2 "
9.0	18.7	56.59 "
Pressure in mm.		
751	13.4	28.45 "
763	19.5	25.79 "

Pressure in mm.	Temperature.	Quantity of magnesium carbonate dissolved by a litre of water.
762	29·3	21·945 grams.
764	46·0	15·7 "
764	62·0	10·35 "
765	70·0	8·1 "
765	82·0	4·9 "
765	90·0	2·4 "
765	100·0	— "

V. H. V.

Anhydrous Gallium Chlorides. By L. DE BOISBAUDRAN (*Compt. rend.*, **93**, 294—297 and 329—331).—Gallium is easily attacked in the cold by dry chlorine, with considerable evolution of heat; this reaction is best effected by passing a current of the gas over the metal enclosed in a horizontal tube of glass subdivided into several sections by drawing it out. To obtain the lower chloride, the reaction is stopped when only a portion of the metal is attacked; by distilling the salt of one section into another, during the passage of the chlorine, the higher chloride is formed. From analyses, the author assigns to the lower chloride the formula of a dichloride, GaCl_2 . The action of water on this chloride is remarkable, and varies with the conditions of experiment. When the salt is exposed to a damp atmosphere, it liquefies quickly and is converted into a thick white syrup with slight evolution of gas; on mixing water with the salt, a flocculent chocolate precipitate is formed, with violent evolution of gas; towards the end of the reaction, the precipitate becomes white, resembling gallium oxide. It appears from this that there exists a gallium oxychloride, intermediate between the sesquioxide and trichloride. Gallium dichloride melts at about 164° , and boils at about 535° , it exhibits the phenomenon of superfusion to a remarkable degree. In the solid state, it forms semi-opaque white crystals, which fuse to a colourless liquid, becoming grey after solidification; this grey colour is always produced when the dichloride is heated, and the author inclines to the belief that this change is due to an isomeric modification. Gallium trichloride, prepared by the process described above, has the composition Ga_2Cl_6 , corresponding with the oxide Ga_2O_3 . This salt melts at $75\cdot5^\circ$, and boils at about $215\text{--}220^\circ$, exhibiting the phenomenon of superfusion even more markedly than the dichloride. In external appearance the crystals of the trichloride resemble those of the dichloride. The salt, when liquefied, absorbs gases very rapidly, which are disengaged in small bubbles at the moment of crystallisation. The vapour-density of the salt was found to be $11\cdot9$ at 273° , theory requiring $12\cdot2$ for the formula Ga_2Cl_6 ; at higher temperatures it appears that the salt is dissociated. Liquid gallium trichloride has a sp. gr. = $2\cdot36$ at 80° , referred to water at the same temperature. Exposed to the air, the salt fumes considerably, and finally deliquesces; the liquid, when evaporated at a gentle heat, dries into an amorphous mass; it then absorbs a further quantity of water, and is converted into a gelatinous substance resembling hydrated silica. V. H. V.

Actinium, a New Metal. By T. L. PHIPSON (*Chem. News*, **44**, 138, also *Compt. rend.*, **93**, 387—388).—The zinc pigment exhibiting the curious actinic phenomenon previously described, is first treated with acetic acid, which dissolves out most of the iron, manganese, magnesium, calcium, and zinc oxide, and then with dilute hydrochloric acid. The residue is well washed, heated with aqua regia, and the solution filtered from undissolved barium sulphate. The filtrate is diluted, mixed with an excess of sodium hydroxide and boiled, zinc oxide remains in solution, whilst actinium oxide is precipitated. The latter is redissolved in hydrochloric acid, and again precipitated with sodium hydroxide; this treatment is repeated two or three times. Finally the actinium oxide is dissolved in a considerable excess of hydrochloric acid, the solution neutralised with ammonia, and filtered from any precipitated ferric hydrate. Ammonium sulphide added to the filtrate throws down actinium sulphide as a bulky canary-yellow precipitate, insoluble in excess of the precipitant, very slightly soluble in acetic acid, but readily soluble in dilute mineral acids. When exposed to direct sunlight it rapidly darkens, finally becoming quite black, but if covered with a piece of ordinary window glass the exposure to light has no effect. Hydrated actinium oxide is a bulky white precipitate, more gelatinous than zinc oxide, only slightly soluble in sodium hydroxide, and not precipitated by ammonia in presence of ammonium salts. It dissolves readily in acids, does not alter when exposed to the air, and is not acted on by light. The anhydrous oxide has a pale fawn-coloured tint, is not volatile, and does not decompose when heated. The zinc pigment employed contained as much as 4 per cent. of the new metal. C. H. B.

Conduct of Finely Divided Iron towards Nitrogen. By I. REMSEN (*Am. Chem. J.*, **3**, 134—138).—The author describes a number of experiments leading to the conclusion that *when iron reduced by hydrogen and certain organic substances is heated with metallic sodium in an atmosphere of hydrogen, a cyanide is readily formed.* The action is similar to that which gives rise to the formation of potassium cyanide in blast furnaces, where the potassium is supplied from the fuel, nitrogen is always present in large quantity, and the iron is constantly passing from the state of oxide to that of metal.

H. W.

Chromammonium Compounds. By O. T. CHRISTENSEN (*J. pr. Chem.* [2], **24**, 74—92).—The author describes a series of compounds derived from the roseochromium compounds (*J. pr. Chem.* [2], **23**, 26), which contain nitro-groups analogous to those of the cobalt compounds; these the author styles xanthochromium compounds.

Xanthochromic Chloride $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}\text{Cl}_4$.—This compound is prepared from purpureochromic chloride, as follows:—20 grams of the chloride are treated with 300 c.c. of water and a few drops of nitric acid, and the solution is heated until all is dissolved. It is then left at rest, and should any unaltered purpureochromic chloride separate out, it is filtered off and treated as before. To the solution of roseochromic chloride obtained in this way, 40—50 grams of pure sodium nitrite and 25 c.c. of dilute hydrochloric acid are added, and the mix-

ture stirred, when a yellow crystalline precipitate of xanthochromium chloride separates out; this is collected, washed with water and with alcohol, and dried at the ordinary temperature. In order to purify it, the chloride is dissolved in water and filtered into a solution of ammonium chloride; the precipitated xanthochloride is collected, washed with water to remove ammonium chloride, then with alcohol, and dried at the ordinary temperature.

Xanthochromic chloride is a yellow crystalline powder composed of microscopic octohedrons; it is more soluble in water than the purpureochromic chloride, and less soluble than the roseochromic compound. Its aqueous solutions are decomposed by exposure to light or by boiling, forming chromic hydroxide. Weak acids liberate nitrous acid from it, and hydrochloric acid converts it into chloropurpureochromic chloride. Sodium hydroxide dissolves it, forming a solution which probably contains xanthochromic hydrate, and from which chromic hydroxide separates on boiling; ammonia is also evolved. Aqueous ammonia has no action on xanthochromic chloride.

Cold aqueous solutions of xanthochromic chloride give the following reactions:—

(1.) With *platinum chloride*, a yellow crystalline precipitate consisting of needles or prismatic crystals. (2.) With *hydrogen fluosilicate*, no precipitate, but the salt is decomposed. (3.) With the *double chloride of sodium and mercury*, a yellowish-red crystalline precipitate. (4.) No precipitates with *ferro- or ferri-cyanide of potassium*. (5.) With *potassium chromate and dichromate*, beautiful yellow precipitates. (6.) With *sodium dithionate*, a yellow crystalline precipitate, consisting of microscopic needles. This reaction is very characteristic for xantho-compounds, and serves to distinguish them from the roseochromic compounds. (7.) With *potassium and ammonium chlorides, potassium bromide, iodide, and nitrate*, precipitates are obtained of the *chloride, bromide, iodide, and nitrate* respectively.

Xanthochromic bromide, $\text{Br}_4(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}$, resembles the chloride in its form and properties, and gives precipitates with *platinum bromide* and the *double bromide of mercury and potassium*.

Xanthochromic iodide, $\text{I}_4(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}$, forms a reddish-yellow precipitate, consisting of red octohedrons. It is sparingly soluble in water, and gives precipitates with *platinum chloride* and *potassium mercuric iodide*.

Xanthochromic nitrate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{NO}_3)_4$, may be prepared by acting on the chloride with potassium or ammonium nitrate, or like the chloride, from roseochromic chloride by substituting nitric acid for hydrochloric acid. It is a yellow crystalline powder, consisting of microscopic octohedrons, is less soluble in water than the chloride. Its reactions with the above reagents are similar to those of the chloride. When boiled with hydrochloric acid it is converted into chloropurpureochromic chloride.

Xanthochromic sulphate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$, is prepared by triturating the chloride with silver sulphate and a little water. It is precipitated from the filtrate by alcohol. It is a yellow crystalline salt, more soluble in water than any of the above salts. Haloid compounds of potassium and ammonium produce precipitates of the xantho-

chrom-haloïd compounds. At 100° , it loses 1 mol. of water, and the second is liberated with decomposition.

Xanthochromic dithionate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{S}_2\text{O}_6)_2 + 2\text{H}_2\text{O}$, may be prepared by precipitating any soluble xanthochromium compound with sodium dithionate. It is a yellow crystalline salt, insoluble in cold water, by which it is partially decomposed on standing, and completely on boiling, into chromium hydroxide. It loses its water of crystallisation at 100° .

Xanthochromic chromate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{CrO}_7)_2$, is a yellow crystalline salt, very sparingly soluble in water, and decomposed by boiling with water, and yields chloropurpureochromic chloride when boiled with hydrochloric acid.

Xanthochromic dichromate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{Cr}_2\text{O}_6)_2$, forms yellow crystalline shining leafy crystals, which resemble lead iodide. It is very sparingly soluble in water, by which it is decomposed in a similar manner to the chromate.

Xanthochromic platinochloride, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}\text{Cl}_4 \cdot 2\text{PtCl}_4$, is obtained as a yellow crystalline precipitate. It is insoluble in water, but dissolves in dilute hydrochloric acid apparently with decomposition. By boiling with concentrated acid, it is converted into chloropurpureochromic chloride.

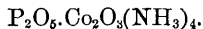
Xanthochromic mercuric chloride, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}\text{Cl}_4 \cdot 4\text{HgCl}_2$, forms a yellowish-red precipitate, consisting of needle-shaped crystals. It is decomposed slowly by water, is soluble in dilute hydrochloric acid, and is decomposed by boiling with this acid.

Xanthochromic Carbonate, $(\text{NO}_2)_2\text{Cr}_2(\text{NH}_3)_{10}(\text{CO}_3)_2$.—This salt has not been analysed, owing to its instability. It is obtained by decomposing xanthochromic chloride with silver carbonate. It is precipitated from the filtrate by addition of alcohol as a yellow crystalline precipitate. It is easily soluble in water, and its aqueous solutions give reactions similar to the chloride.

Xanthochromic Hydroxide.—An alkaline solution of this compound is obtained by triturating the chloride with moist silver oxide. Its solution produces precipitates in solutions of metallic salts like the alkalis, and xantho salts are obtained by neutralisation with acids. Potassium hydroxide is formed, and ammonia liberated when the solution of the hydroxide is added to potassium or ammonium chloride.

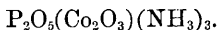
P. P. B.

Cobaltamines. By PORUMBARU (*Compt. rend.*, **93**, 342—345).—When the hydrogen and normal roseocobaltamine pyrophosphates are heated in sealed tubes at 175° in presence of water they lose ammonia, and are converted into an insoluble phosphate of the formula



This salt crystallises in blue rectangular plates; when treated with hydrochloric acid, it is decomposed into cobalt and luteocobaltamine chlorides. If the pyrophosphate is heated at 225° instead of 175° , violet crystals are obtained, $\text{P}_2\text{O}_5(\text{CoO})_2\text{N}_2\text{H}_6\text{O} + \text{H}_2\text{O}$, soluble in cold hydrochloric acid, and reprecipitated by ammonia, but redissolved by excess of the latter. This ammoniacal solution absorbs oxygen from the air, and is converted into oxycobaltic chloride and phosphate

of formula $P_2O_5[Co_2O_4(NH_3)_{10}]$. By deoxidation this phosphate is converted into a brick-red roseocobaltamine phosphate, of formula $P_2O_5[Co_2O_3(NH_3)_{10}]$, which, heated in sealed tubes, is converted into a double phosphate of cobalt and roseocobaltamine of formula



The luteocobaltamine pyrophosphate undergoes the same series of reactions. The author remarks that in the different phosphates and pyrophosphates the groupings $Co_2O_3(NH_3)_{12}$ and $Co_2O_3(NH_3)_{10}$ take the place of $3H_2O$, and the same property is noticeable in the nitrates, sulphates, and other salts studied by Frémy. It appears that the groupings $Co_2(NH_3)_{10}$ and $Co_2(NH_3)_{12}$ act as trivalent radicals.

V. H. V.

Action of Arsenic and Phosphoric Acids on Sodium Tungstates, and a New Method of Analysing Tungstates.

By J. LEFORT (*J. Pharm. Chim.* [5], 4, 221—224).—Phosphoric and arsenic acids appear to act on alkaline tungstates in a manner similar to that of the organic acids. In order to estimate tungstic acid the author employs a solution of quinine sulphate or acetate. The solution of the alkaline tungstate is acidified with nitric acid, quinine solution added, and the liquid left at rest. The precipitate is filtered off, washed with cold water, dried, and ignited at a red heat, with frequent addition of a few drops of concentrated nitric acid. The residue is tungstic acid. Alkaline mono-, di-, tri-, and meta-tungstates give strictly corresponding quinine compounds, and it is thus possible to ascertain, from the percentage amount of tungstic acid in the precipitate, the nature of the tungstate analysed. At 10° , a hundred parts of water dissolve—

Quinine monotungstate	0.040 part.
„ bitungstate	0.012 „
„ tritungstate	0.011 „
„ metatungstate	0.008 „

The solubility of the quinine salt decreases as the proportion of acid increases. When sodium mono- or bi-tungstate is heated with a large excess of tungstic acid, no tungstate is produced containing relatively more acid than the quadri- or meta-tungstate.

C. H. B.

Action of Oxygen on Mercury at the Ordinary Temperature. By E. AMAGAT (*Compt. rend.*, 93, 308).—The author has varied his experiments which led him to maintain, contrary to the generally received opinion, that dry mercury and dry oxygen have no action one on another, and has arrived at the same result (compare this vol., p. 782). Inasmuch as this received opinion is based on a statement of Regnault, in his memoir on the compressibility of gases, the author quotes a passage from the later works (*Œuvres*, 2, 237), to show that Regnault himself contradicts the error promulgated in the various text-books.

V. H. V.

Mineralogical Chemistry.

Mineralogical Notices. By B. SILLIMAN (*Sill. Am. J.* [3], **22**, 198—205).—This paper contains descriptions: (1) Of vanadates and other minerals from Arizona.—(a.) *Vanadinite*, ($\text{PbCl}_2, 3\text{Pb}_3\text{V}_2\text{O}_8$), occurs in comparative abundance in the “Silver District” of Yuma County, Arizona, in the Hamburg, Princess, and Red Cloud Mines, forming small but beautiful crystals, having an orange-red, reddish-yellow, or bronze colour, and high lustre. It is found also in the “Vulture District,” between the Hassayampa river on the west, and Agua Fria on the east, and extending in a north and south direction from the Vulture Mine to the Antelope Mountains; further in Farley’s “Collateral Mine,” about 20 miles north-east of Vulture; and in the Montezuma lead-mine, 11 miles east of Vulture and south-east of Collateral, in drusy crusts of a deep yellow and brown colour on masses of cerussite.

Descloizite (?), $\text{PbCl}_2, 30\text{Pb}_3\text{V}_2\text{O}_7$ (?).—A mineral which may prove to be identical with this, occurs amongst the ores of the Collateral Mine, in blue-black and brownish-black, semi-transparent and very brilliant crusts, the individuals being imperfectly developed. Hardness about 3—3·5; streak, yellow to brownish-yellow. It reacts very strongly for vanadium and lead, and exhibits the reactions of copper, manganese, and zinc. Heated in a closed tube it melts and gives off water.

Volborthite (?).—A specimen provisionally referred to this species was found amongst the products from the Collateral Mine, forming small botryoidal masses, adhering to the polished faces of deep red quartz crystals. In thin scales the mineral is transparent and of a clear olive-green colour. Lustre, vitreous and dull. Streak, bright yellow. No crystals were detected. Heated alone in a tube, it melts readily and adheres to the glass, but does not give off water. Dissolves in dilute hydrochloric acid to a greenish solution, from which alcohol throws down tufts of lead chloride. On charcoal, it fuses to a black shining bead, which gives off lead fumes, and exhibits copper when crushed. With soda, it gives a bead of lead, enclosing copper. On gently heating the assay, the charcoal becomes stained with zinc oxide.

An anhydrous cryptocrystalline mineral containing vanadium, occurs amongst the “Collateral” ores. It varies in colour from light yellow to black-brown; gives the reactions of Domeyko’s *chileite*, but is not a clay-like mineral. It readily yields a globule of lead containing copper.

Mottramite (?).—To this species perhaps belongs a hydrated mineral, very rich in vanadic acid, and giving the reactions of lead, copper, and chlorine, which occurs in amorphous yellow-green masses at “the Frenchman’s Mine” in a deeply iron-stained gold-bearing quartz vein, about 18 inches thick. The same vein contains a buff-coloured substance rich in vanadinite.

Mimetite or *Mimetesite*, $\text{PbCl}_2 \cdot 3\text{Pb}_3\text{As}_2\text{O}_8$, occurs in considerable masses north of the Domingo Mine, on Castle Creek, in the extreme north-west of the Vulture District.

Wulfenite (lead molybdate) occurs at the Red Cloud Mine, in large very solid tabular crystals, having a rich orange-yellow to orange-red colour and brilliant lustre. In the Melissa Mine in Silver District, adjacent to the Red Cloud, wulfenite is found in octagonal prismatic crystals, having a pure orange-red colour. The Rover Mine in the same district yields wulfenite of a somewhat lighter orange-red colour.

Crocoite-group.—Three, if not four, of the species of this group, occur amongst the ores of the Vulture region, especially in the "Collateral" and "Chromate" veins. These two veins, together with the "Blue Jay" and the "Phoenix Mine," form a group of singular mineralogical interest, furnishing, among more common minerals, the species crocoite, phœnicochroite, vauquelinite, joassite (?), vanadinite, volborthite (?), descloizite (?), chileite (?), and wulfenite. *Vauquelinite*, $\text{Pb}_2\text{CuCr}_2\text{O}_9$, occurs abundantly, associated with galeinite and crocoite, in a gold quartz gangue or veinstone. The genesis of the chromate is very manifest. The nucleus of unaltered gehlinit is surrounded with a bright pea-green and apple-green areola of vauquelinite, sometimes semi-transparent and uncrySTALLINE; and this green mass is succeeded by crystalline and transparent crocoite of orange-red and cinnabar-red colour. Besides the associated species just named, there also occur cerussite, gold, and magnetite.

2. *Thenardite*, Na_2SO_4 , from the Rio Verde, Arizona Territory.—This mineral occurs in large masses, some of which, in the rough, form distinct crystals with imperfect faces, showing eminent cleavage in the direction of the basal plane of the prism, and a hackly cleavage in the opposite direction. Hardness below that of calcite. Lustre vitreous. Fracture conchoidal to hackly. Analysis gave:

	Cl.	SO_3 .	CaO.	MgO.	Na_2O .	Insol.
I.	0.095	56.410	0.120	0.021	[42.964]	0.390 = 100
II.	0.097	56.310	0.130	0.023	[43.070]	0.370 = 100

The mineral is therefore nearly pure anhydrous sodium sulphate, the formula $\text{Na}_2\text{O}, \text{SO}_3$ requiring 43.82 per cent. Na_2O and 56.18 SO_3 . The insoluble matter, chiefly clay, gives it a prevailing shade of yellowish-grey. This thenardite is used for the salting of cattle, the animals resorting to it freely, licking it as they are wont to lick common salt, and with good results. Thenardite has also been found in Nevada and elsewhere in the arid regions of the West Coast, but not hitherto in sufficient quantity to be of commercial importance. According to G. vom Rath, thenardite occurs very abundantly on the flat shores of Lake Baikal in Central Asia.

H. W.

Notes on Mineral Localities in North Carolina. By W. E. HIDDEN (*Sill. Am. J.* [3], 22, 21—25).—*Monazite* occurs at Millholland's Mill, Alexander County, in minute crystals imbedded in garnetiferous mica-schist, and associated with muscovite, quartz, and rutile. The crystals of monazite rarely exceed $\frac{1}{4}$ inch in length, and

$\frac{1}{20}$ th inch in diameter; they appear transparent and of topaz colour under the microscope, and their faces have a strong lustre. They are uniformly long prismatic with modified terminations, the prism having the shape of an acute rhomboid. Monazite occurs also in Burke Co., in Mitchell Co., at the Deake mica mine, and in Yancey Co., at the Ray mica mine on Hurricane Mountain.

Uraninite (pitchblende) occurs at the Deake, Lewis, and Flat Rock mica mines in Mitchell Co., in pure and unaltered masses, sometimes weighing several pounds. Cubes and cubo-octohedrons imbedded in feldspar were obtained at the Deake mine, having a thin coating of uranotil or gummite. Some of the uraninite masses had a submetallic lustre, and much of it was devoid of pitchy appearance. *Gummite*, *uranotil*, and *uranochre* occur at the above mines in considerable abundance, and are so intimately associated as to be inseparable. Pseudomorphs (cubes and octohedrons) after uranite are quite common. According to Genth, this North Carolina gummite is a mixture of uranic hydroxide, uranotil, lead uranate, and barium uranate. Some of it is very beautiful, varying in the same specimen from a bright lemon-yellow to deep orange-red, and often with a core of velvet-black uraninite.

Aeschynite (?).—A mineral much resembling this species occurs in large well-defined deeply striated prisms at Ray's mica mine, imbedded in feldspar and associated with apatite and beryl.

Samaraskite is found in Mitchell Co. in masses weighing several pounds. Associated with it is a light brown, resinous-looking mineral of high specific gravity, which may be massive hatchettolite or a new species.

Figures and descriptions of quartz-crystals and beryls from Alexander Co. are also given in this paper. H. W.

Spanish Minerals. By F. A. GENTH, JUN. (*Am. Chem. J.*, 1, 323—326).—1. *Cobaltiferous Gersdorffite* from Benahanis, Province of Malaga, where it occurs in a gangue of white crystalline calcite, and often so intimately mixed therewith, that the two appear to form only one mineral of a light grey colour. On placing the mixture in dilute hydrochloric acid, the calcite dissolves, and the gersdorffite remains as a very fine crystalline powder. Granular, massive. H. = 4. Sp. gr. = 5.856. Lustre metallic, but somewhat tarnished. Streak greyish-black, colour grey. Before the blowpipe in the closed and open tube, it gives the reactions of arsenic and sulphur; is reduced on charcoal to a white, bright brittle globule; and when treated with successive portions of borax, gives the reactions of iron, cobalt, and nickel. Nitric acid decomposes it, with separation of sulphur and arsenious oxide, and formation of a brownish-green solution. Analysis gave—

S.	As.	Fe.	Ni.	Co.	Cu.
22.01	39.71	1.12	24.83	12.54	0.25 = 100.46

agreeing with the formula $R(S,As)$, in which $Ni:Co = 2:1$ and $S:As = 14:11$. Associated with the gersdorffite are chalcopyrite, erythrite, pharmacolite, lavendulite, olivenite, and aragonite.

2. *Jamesonite*, from the Province of Huelva. Indistinctly crystalline, the particles showing lamination. Massive. Fracture uneven. $H. = 2.5$. Sp. gr. = 5.467. Soils paper. Lustre metallic. Colour dark steel-grey. Streak almost black. Opaque. The mineral appears to be homogeneous, excepting that a considerable quantity of pyrites is disseminated throughout the mass. There is also present a soft yellowish-white mineral, with waxy lustre, which was not further examined. Analysis gave—

Fe.	Ag,Cu.	Pb.	Sb.	S.
5.95	0.28	38.29	33.15	23.60 = 101.27

This gives the formula $(Pb,Fe)_2Sb_2S_5$, together with a small quantity ($\frac{1}{15}$) of pyrites. Deducting this, the pure mineral has the following composition:—

Sb.	S.	Pb.	Fe.
34.03	22.31	38.49	5.16 = 99.99

H. W.

Dufrenite from Rockbridge Co., Virginia. By J. L. CAMPBELL (*Sill. Am. J.*, [3], 22, 65).—This mineral occurs in a mine of the Blue Ridge range, partly in irregular nodules, partly as incrustations on the surface of an underlying bed of limonite. The freshly broken surface shows a rather dull silky lustre and dark greenish-brown (almost black) colour. By long exposure to the weather, the colour changes to yellowish, like that of fibrous limonite. The unaltered mineral yields a powder of a light yellowish-green colour. It gives off water when heated in a tube, and small fragments heated to bright redness for a short time assume a bright reddish chestnut-brown colour when cold. Before the blowpipe, the mineral fuses readily to a black magnetic bead, and gives with borax well marked reactions of iron, with some indications of manganese. Sp. gr. = 3.382. $H. = 4$. Analysis gave—

P ₂ O ₅ .	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O. ⁽¹⁾	SiO ₂ . ⁽²⁾
31.76	6.14	50.85	0.21	0.40	1.12	0.76	8.53	0.12 = 99.89

¹ Given off at a red heat.

² Insoluble; very fine sand.

H. W.

Meteoric Iron of Unknown Locality, in the Smithsonian Museum. By C. U. SHEPARD [*Sill. Am. J.* [3], 22, 119).—This mass is oval in form, with three or four prominent knobs, and weighs about six pounds. A fragment separated by the hammer exhibited a crystalline structure, the broken surfaces being covered with an extremely thin micaceous layer of schreibersite. The fragment, after polishing, had a somewhat whiter colour than artificial iron; when etched, it showed a somewhat homogeneous finely crystalline texture, and became still whiter. The surface viewed at fixed angles of reflection glimmered simultaneously, like that of sunstone oligoclase, indicating that the crystallisation of the general mass was probably that of a single individual. The etched surface is obscurely banded in some portions with bars about $\frac{1}{20}$ inch thick, and has a

thickly dotted or punctate character, the dots being very bright, and slightly concave. On the whole, therefore, this iron differs in structure from any meteoric iron yet known. Its sp. gr. is 7.589. Its analysis gave 92.923 per cent. Fe, 6.071 Ni, 0.539 CO, and 0.562 schreibersite (iron phosphide) = 100.095, with traces of copper and tin. The polished surface showed no tendency to deliquesce.

H. W.

Chalybeate Spring, Kingstead, St. Edmunds. By W. JOHNSTONE (*Chem. News*, **44**, 140).—The water was collected in October, 1880. Sp. gr. = 1.1465*; temperature 11.7°, that of the air being 11.1°.

	Parts per 1000.	Grains per gallon.
Calcium sulphate	0.01550	1.0850
„ phosphate	0.00419	0.2933
„ carbonate	0.22882	16.0174
Magnesium bromide	0.00144	0.1008
„ chloride	0.00053	0.0371
„ carbonate	0.02719	1.9033
Potassium chloride	0.00056	0.0392
Sodium chloride	0.03157	2.2099
Ferrous carbonate	0.01190	0.8330
Silica	0.01942	1.3594
	<hr/> 0.34113	<hr/> 23.8784
Carbonic anhydride	24.422 c.c.	6.507 cb. ins.
Nitrogen	32.806 „	8.776 „
Oxygen	5.236 „	1.400 „
	<hr/> 62.464	<hr/> 16.613

Traces of lithium and strontium, free and albuminoid ammonia, and crenic and apocrenic acids were also present.

C. H. B.

Ferruginous Carbonated Waters. By J. VILLE (*Compt. rend.*, **93**, 443—445).—The author has studied the solubility of metallic iron in water charged with carbonic acid, and has arrived at results differing from those of Hauer. The latter obtained at ordinary temperature and pressure a solution containing 0.219 gram carbonate of iron per litre, whereas the author obtained after 24 hours at 29° a solution containing 0.704 gram of the carbonate, the quantity dissolved increasing regularly with the time. The strength of the solution also increases with decrease of temperature. The author has also studied the action of various salts on the ferruginous water. The carbonates of the alkalis and alkaline earths precipitate hydrated ferric oxide from this water, and are themselves converted into bicarbonate, hence the bicarbonates have no action on the water.

The chlorides and sulphates retard the decomposition of the waters by the air. The results obtained in the case of artificial waters are

* The sp. gr. as here given is considerably higher than that of such waters as the Harrogate waters, which contain a very much larger quantity of solid matter.

confirmed by Moitessier's analyses of natural waters, which show that the richness of carbonate of iron is inversely as the quantity of alkaline carbonate which they contain. The action of calcium carbonate mentioned above offers an explanation of the deposits of limonite in calcareous soil.

V. H. V.

Organic Chemistry.

Heat of Combustion of Heptane and Hexhydrotoluene.

By W. LOUGUININE (*Compt. rend.*, **93**, 274—276).—The *heptane* used for this research, was obtained by the fractional distillation of American petroleum; the determination presented some difficulty on account of the volatility of the hydrocarbon, which caused portions of the vapour to pass over unburnt. As a mean of several determinations, the author found for C_7H_{16} (liquid) + $22O$ (gas) = $7CO_2$ (gas) + $8H_2O$ (liquid) the value 1137450 cal. From the numbers obtained as compared with those of Berthelot for ethane and propane, the author considers that the increase of heat of combustion for every CH_2 grouping decreases in proportion as the hydrocarbon molecule becomes more complex.

The *hexhydrotoluene* was extracted from Caucasus petroleum; the author found for C_7H_{14} (liquid) + $21O$ (gas) = $7CO_2$ (gas) + $7H_2O$ (liquid) the value 1095030. On comparing the heats of combustion of heptane, C_7H_{16} , and hexhydrotoluene, there is found a difference of 42420, which corresponds to the differences between those of propane and propylene (46200 cal.) and of ethane and ethylene (47400 cal.). These values are, however, less than the heat evolved in the combustion of $2H$, consequently there is an evolution of heat in the fixation of $2H$ on the hydrocarbons of the olefine series. V. H. V.

Hexylene from Mannitol. By J. DOMAC (*Monatsh. Chem.*, **2**, 309—322).—The author finds that this hexylene, when oxidised by potassium permanganate or by nitric acid, yields acetic and normal butyric acids, and hence infers that it has the normal constitution—



a result previously arrived at by Hecht (*Ber.*, **11**, 1152; this Journal, 1878, Abstr., 962).

For the preparation of secondary hexyl iodide from mannitol, the author finds that it is best to use only 75 g. iodine to 50 g. mannitol, which is equivalent to 1 mol. mannitol to 2 mols. HI (instead of the 383.8 g. iodine recommended by Erlenmeyer and Wanklyn), then add 130 c.c. water, and as much ordinary phosphorus as is required to prevent the separation of iodine. The iodine and water are gently heated in a tubulated retort, and phosphorus is added till the whole of the iodine is converted into colourless hydriodic acid; 25 g. mannitol is then added, and the distillation is carried on in a stream of carbonic

anhydride as long as hexyl iodide continues to pass over. The retort is then left to cool, and another 25 g. mannitol is added; the hydriodic acid which has distilled over is poured back; and the distillation then carried on to the end, a little phosphorus being added occasionally, if the contents of the retort become brown from separation of iodine.

By this method of proceeding, the product of hexyl iodide amounts to 85 to 95 per cent. of that required by theory; with the larger proportion of iodine recommended by Erlenmeyer and Wanklyn, the author finds that a considerable proportion of the mannitol becomes carbonised. Together with the iodide, there is always formed a small quantity of a yellowish viscid liquid—perhaps a phosphoric ether—which remains in the residue, dissolves easily in alcohol and ether, but is insoluble in water.

The corresponding *hexylene chlorhydrin*, $C_6H_{12}Cl(OH)$, is produced by adding 40 g. hexylene to a solution of hypochlorous acid recently prepared by agitating mercuric oxide suspended in water with chlorine gas. When purified by washing with water, distillation with steam, and dehydration with calcium chloride, it is a colourless liquid, heavier than water, and having a peculiar not unpleasant odour; it is decomposed by distillation in the ordinary way. By reduction with iron filings and acetic acid, it is converted into secondary hexyl alcohol (methylbutyl carbinol) identical with that obtained directly from the iodide.

H. W.

Action of Sulphuric Acid on Bromamylene. By G. BOUCHARDAT (*Compt. rend.*, **93**, 316—318).—On mixing together concentrated sulphuric acid and bromamylene (b. p. 115°), a considerable rise of temperature takes place; and the mixture, after the reaction is complete, separates into two layers, the lower of which consists to a large extent of amylene bromide (b. p. 175 — 180°) $C_5H_{10}Br_2$. On adding water to the higher layer, an oil separates out, which on distillation boils at about 76 — 81° , and has a sp. gr. = 0.832 . This body, $C_5H_{10}O$, has all the properties of a ketone. It appears, then, that the action of sulphuric acid on bromamylene abstracts a molecule of hydrobromic acid, with formation of valerylene; at the same time, a portion of the undecomposed bromamylene takes up the liberated hydrobromic acid, and forms amylene bromide, while the valerylene fixes a molecule of water, and yields the acetone. The action of dilute sulphuric acid (1 : 1) on bromamylene differs from that of the concentrated acid; instead of a ketone, a body having the properties of an alcohol is produced.

V. H. V.

Nitro-olefines. By L. HATTINGER (*Monatsh. Chem.*, 1881, 286—294).—The author in 1878 (this Journal, 1879, Abstr., 700) obtained nitrobutylene by the action of nitric acid on trimethylcarbinol, and he has since been engaged with the further examination of this body and some of its homologues.

Nitrobutylene may also be prepared by direct nitration of isobutylene; but the yield is not satisfactory, a considerable portion of the hydrocarbon being oxidised to carbonic anhydride, fatty acids and acetone, and a small quantity of a white crystalline substance being sometimes also formed, having the composition $C_4H_8(NO_2)_2$ [butylene

dinitrite]? probably homologous with the amylene dinitrite, $C_6H_{10}(NO_2)_2$, which Guthrie obtained by the action of fuming nitric acid or nitrogen tetroxide on amylene, and with Semenov's ethylene nitrite, $C_2H_4(NO_2)_2$, produced by the action of nitrogen tetroxide on ethylene.

When nitrobutylene is heated for several hours at 100° in a sealed tube, with four or five times its volume of strong hydrochloric acid, and the contents of the tube are subsequently evaporated to dryness, the water which distils over being frequently poured back, a residue is finally obtained, consisting of the hydrochlorides of ammonia and hydroxylamine. On boiling the united distillates in a reflux apparatus with barium carbonate, small quantities of neutral volatile bodies—probably acetone and condensation-products thereof—are driven over with the steam; and on exhausting the concentrated solution of the barium salts with alcohol, a salt is obtained, the acid of which exhibits all the characteristic properties of α -hydroxybutyric acid, excepting that its melting point is rather too low (65° instead of 75.7°).

The action of hydrochloric acid on nitrobutylene appears therefore to be analogous to that which it exerts upon the nitroparaffins, excepting that hydrochloric acid is added on to the product, and the resulting α -chlorisobutyric acid is converted by the subsequent boiling with water and barium carbonate into α -hydroxyisobutyric acid. The water also exerts a decomposing action, resulting in the formation of nitromethane, which by further action is converted into formic acid and acetone; and the latter, by the condensing action of the hydrochloric acid, is converted into the neutral bodies above-mentioned. The formation of ammonia has not yet been explained.

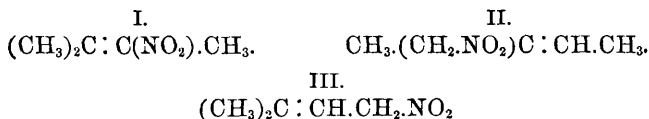
Nitroamylene, $C_6H_9NO_2$, is best obtained by nitration of dimethyl-ethylcarbinol, the process being conducted in the same manner as for the preparation of nitrobutylene from trimethylcarbinol. On washing the product with water and distilling it under ordinary pressure, the nitroamylene passes over between 160° and 170° . Considerable decomposition, however, takes place at the same time, resulting in the formation of nitrogen oxides, acetone, and perhaps also of nitroethane.

Nitroamylene is an oily liquid, having a faint yellow colour, and a peculiar, powerful odour; a little heavier than water, and insoluble therein, but miscible in all proportions with alcohol and ether. It is very slowly dissolved by potassium hydroxide, and the solution treated with potassium nitrite and sulphuric acid distinctly exhibits the blue reaction described by V. Meyer, together with a very faint red coloration. With alcoholic soda it forms a yellow precipitate containing a quantity of sodium much greater than that which corresponds with the evaporation of sodium-nitroamylene. *Bromine* unites with nitroamylene, forming a crystalline dibromide, but the reaction is not quite definite, inasmuch as hydrogen bromide is formed at the same time. *Stannous chloride* appears to remove the nitrogen of nitroamylene chiefly in the form of hydroxylamine, but the product when heated with chloroform and alcoholic potash also yields a distinct carbylamine reaction, indicating the presence of an amine.

Nitroamylene heated with 20 times its volume of *water* at 100° in a sealed tube for thirty hours, yields nitroethane, $C_2H_5.NO_2$ (con-

vertible by reduction into amidoethane or ethylamine), and a ketone recognisable by the bisulphite reaction, that is to say, a splitting up of the molecule takes place at the double linking (see formula below). On heating nitroamylene for 15 hours with 5 or 6 vols. strong *hydrochloric acid*, a considerable quantity of a brown resin is separated, and on repeatedly distilling the product with water, a distillate is obtained containing acetic acid, together with a residue consisting mainly of ammonium chloride, but exhibiting also, though very faintly, the reactions of hydroxylamine. Hence it appears that the action of hydrochloric acid on nitroamylene consists in a complete splitting up of the molecule.

The wash-waters of the crude product of the nitration of dimethyl-ethyl carbinol contain,—together with small quantities of volatile fatty acids, oxalic acid and dimethyl ketone,—a small quantity of an amylene, which dissolves easily in dilute sulphuric acid (1 pt. H_2O to 2 pts. SO_4H_2), and is therefore probably trimethylethylene; and as this hydrocarbon is easily formed from the tertiary pentyl alcohol employed for the preparation of the nitroamylene, it may probably be regarded as the mother-substance of this nitro-compound, which must accordingly be represented by one of the three following constitutional formulæ—



the first of which is the most probable, inasmuch as substituted groups always attach themselves to the least hydrogenised atoms of carbon. A confirmation of this formula is moreover afforded by the production of the blue colour-reaction above mentioned, and in the mode of splitting up of the molecule under the influence of water and of hydrochloric acid.

Action of Nitric Acid on Ethylene.—Akestorides (*J. pr. Chem.*, **15**, 64) found that ethylene is completely absorbed by fuming nitric acid, with formation of oxalic acid; and Kekulé (*Ber.*, **2**, 329) obtained with ethylene and nitrosulphuric acid, a body having the composition $C_2H_4N_2O_5$. Haitinger, by passing ethylene into a Butlerow's absorption-tube containing fuming nitric acid, obtained a small quantity of an extremely decomposable oily product, which often split up suddenly, with copious evolution of gas, and formation of a pulp of crystals of oxalic acid. This product appears to be a mixture, inasmuch as potassium hydroxide dissolves only a portion of it ($\frac{1}{2}$ to $\frac{3}{4}$). The oil also decomposes spontaneously at ordinary temperatures, and suddenly, with violent evolution of gas, when an attempt is made to distil it. H. W.

Lead, Cadmium, and Mercury Oxycyanides. By JOANNIS (*Compt. rend.*, **93**, 271—274).—The author has already indicated the existence of a calcium oxycyanide.

Lead Oxycyanide.—The white precipitate formed by potassium cyanide in dilute lead acetate, is not lead cyanide, as hitherto supposed, but an oxycyanide. This compound dried in a vacuum has the composition $2\text{PbO}, \text{Pb}(\text{CN})_2, \text{H}_2\text{O}$; it is insoluble in water. Its heat of formation was ascertained by decomposing it with dilute nitric acid. It was found that the reaction $2\text{PbO}, \text{Pb}(\text{CN})_2, \text{H}_2\text{O} + 3\text{N}_2\text{O}_5$ (dilute), $= 3(\text{PbO}, \text{N}_2\text{O}_5)$ (dissolved) + 2HCN (dissolved) disengages 36·8 cals., whence $\text{Pb} + 2\text{CN} + 2\text{PbO} + \text{H}_2\text{O}$ (solid) $= 2\text{PbO}, \text{Pb}(\text{CN})_2, \text{H}_2\text{O}$ disengages 36·8 cals. This body cannot be dehydrated without loss of hydrocyanic acid. Similarly the action of hydrocyanic acid on lead monoxide, and various other reactions supposed to give the cyanide, yield not this salt, but the oxycyanide.

Cadmium Cyanide.—By precipitating a saturated solution of cadmium sulphate with a concentrated solution of potassium cyanide, cadmium cyanide is formed. On dissolving this salt in dilute hydrochloric acid, it was found that $\text{Cd}(\text{CN})_2 + 2\text{HCl}$ (dilute) $= \text{CdCl}_2$ (dissolved) + 2HCN (dissolved) disengages 5·8 cals., whence $\text{Cd} + \text{C}_2\text{N}_2$ (gas) $= \text{Cd}(\text{CN})_2$ (solid) disengages 39·6 cals.

Cadmium Oxycyanide.—This compound is obtained by treating cadmium oxide with hydrocyanic acid; dried in a vacuum, it has a composition $2\text{Cd}(\text{CN})_2, \text{CdO}, 5\text{H}_2\text{O}$. Its heat of formation was found by decomposing it with dilute sulphuric acid. The equation $2\text{Cd}(\text{CN})_2, \text{CdO}, 5\text{H}_2\text{O} + 3\text{SO}_3$ (dilute) $= 3\text{CdOSO}_3$ (dissolved) + 4HCN disengages 12·6 cals., whence $2\text{Cd}(\text{CN})_2, \text{CdO}, 5\text{H}_2\text{O}$ (solid) $= 2\text{Cd}(\text{CN})_2, \text{CdO}, 5\text{H}_2\text{O}$ disengages 22·8 cals.

Mercury Oxycyanide, $\text{Hg}(\text{CN})_2, \text{HgO}$.—This compound is already known; it is obtained by warming a concentrated solution of mercuric cyanide in the presence of excess of mercury; when heated to 135° , it decomposes with explosion. Berthelot has found the heat of formation of mercuric cyanide to be 23·4; hence HgO (solid) + 2HCN (solid) $= \text{HgO}, \text{Hg}(\text{CN})_2$ (solid) disengages 2·4 cals.

Mercury Oxycyanide, $3\text{Hg}(\text{CN})_2, \text{HgO}$.—This compound has been obtained by warming 5 parts of mercuric cyanide, and 2 of the oxycyanide, $\text{Hg}(\text{CN})_2, \text{HgO}$, in presence of a sufficient quantity of water to form a cold solution. Like the former oxycyanide, it decomposes explosively. The heat of formation in the reaction $3\text{Hg}(\text{CN})_2$ (solid) + HgO (solid) $= 3\text{Hg}(\text{CN})_2, \text{HgO}$ (solid) disengages 9·8 cals.

V. H. V.

Determination of the Reaction-Values of the Components of Alcohols and Acids. By N. MENSCHUTKIN (*J. pr. Chem.* [2], 49—74).—All monohydric alcohols may be regarded as derived from methyl alcohol, by substituting for one or more atoms of hydrogen, some univalent radicle. Thus primary alcohols have a general formula $\text{CH}_2\text{R}.\text{OH}$, secondary alcohols $\text{CHR}_2.\text{OH}$, and tertiary alcohols $\text{CR}_3.\text{OH}$. These general formulæ are thus composed of a constant and a variable group, which the author styles the components of the alcohols. He proposes to determine the "reaction-values" of these components by comparing the etherification data of the different alcohols and acetic acids, with those of methyl alcohol and acetic acid. An account of the method of determining the initial velocity and limit of etherification, and many of the results obtained

have already appeared in this Journal (vol. 36, 214—215; 215—216; vol. 38, 36—38, 39, 147).

The etherification data of methyl alcohol and acetic acid are taken as 100 for the limit, and 80 for the initial velocity. This means that from an equal number of molecules of methyl alcohol and acetic acid, 100 mols. are neutralised before equilibrium is established; and that 80 of these are neutralised in the first hour.

Monohydric Alcohols.—(1.) *Primary Alcohols.*—The following table contains the etherification data of several primary alcohols and acetic acid, expressed in terms of the above standard:—

	Velocity.	Limit.
Methyl alcohol, HCH_2OH	80.0	100.0
Ethyl „ MeCH_2OH	67.3	95.6
Propyl „ EtCH_2OH	66.9	96.0
Normal butyl alcohol, PrCH_2OH	67.4	96.6
Isobutyl „ $\text{IsoPrCH}_2\text{OH}$	64.6	96.6
Normal octyl „ $\text{C}_7\text{H}_{15}\text{CH}_2\text{OH}$	67.0	?
Allyl „ $\text{C}_2\text{H}_3\text{CH}_2\text{OH}$..	51.9	85.3
Propargyl „ $\text{C}_2\text{HCHCH}_2\text{OH}$..	29.5	?
Benzyl „ $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$..	54.6	87.3

The “reaction-value” of a component, *e.g.*, methyl and ethyl groups, is determined by subtracting the etherification data of ethyl and propyl alcohol from those of methyl alcohol; thus the following values are obtained:—

	Velocity.	Limit.
Methyl, Me	— 12.7	— 4.4
Ethyl, Et	— 13.1	— 4.0

In this manner it is shown that the substitution of a univalent radicle in methyl alcohol reduces the power of etherification, and that the reaction-values of the normal hydrocarbon radicles is practically the same. A similar comparison of normal butyl and isobutyl alcohols shows that isomerism in the radicle does not influence the limit, but reduces the velocity of etherification. The unsaturated alcohols are characterised by comparatively lower limit and velocity, and an unsaturated hydrocarbon radicle has a lower “reaction-value” than the corresponding saturated one, and further that this decreases with loss of hydrogen. Thus the reaction-value of vinyl, C_2H_3 , is less than that of ethyl, and that of acetenyl, C_2H , less than that of vinyl.

Experiments with monochlorhydrin of glycol and dibromhydrin of glycerol show that the substitution of haloid elements is unfavourable to the formation of ethers.

Experiments have shown that the etherification data of ethyl and isobutyl alcohols with acetic, caproic, and butyric acids are practically identical. Hence the above reaction-values, although determined for acetic acid alone, have a more general signification.

(2.) *Secondary Alcohols.*—The following table contains the etherification data of several secondary alcohols with acetic acid, expressed in terms of methyl alcohol and acetic acid:—

	Velocity.	Limit.
Dimethyl carbinol, $\text{Me}_2\text{CH.OH}$	38.2	86.9
Methyl ethyl carbinol, MeEtCH.OH	32.5	85.2
Diethyl ,, $\text{Et}_2\text{CH.OH}$	24.3	84.2
Isopropyl methyl carbinol, $\text{C}_3\text{H}_7\text{MeCH.OH}$.	27.2	85.2
Isobutyl ethyl ,, $\text{C}_4\text{H}_9\text{EtCH.OH}$.	26.2	?
Hexyl methyl ,, $\text{C}_6\text{H}_{13}\text{MeCH.OH}$	34.1	?
Ethyl vinyl ,, $\text{EtC}_2\text{H}_3\text{CH.OH}$.	21.3	75.1
Diallyl ,, $(\text{C}_3\text{H}_5)_2\text{CH.OH}$.	15.3	72.0
Ethyl phenyl ,, EtPhCH.OH ..	27.2	?
Diphenyl ,, $\text{Ph}_2\text{CH.OH}$	31.6	?

It is thus seen that secondary alcohols have a lower velocity and limit of etherification than primary alcohols, and that the limit is some 10 units less than that of primary alcohols. It will also be seen that the presence of unsaturated hydrocarbon radicles has a similar influence in secondary alcohols to that shown in the case of primary alcohols. By a method similar to that used in the case of primary alcohols, the reaction-values of the "variables" or hydrocarbon radicles in secondary alcohols are deduced, and it is shown that the reaction-value of the same "variable" is always the same; further, that the same radicle has a smaller reaction-value in a secondary as in a primary alcohol, and that in secondary alcohols the reaction-value of the radicle is influenced by the number of carbon-atoms it contains.

(3.) *Tertiary Alcohols*.—The author has already shown (this Journal, **36**, 215—216) that tertiary alcohols do not exhibit normal etherification, and that the limit cannot be determined; the initial velocity, however, may be determined; for trimethyl carbinol it was found to be 2, hence the reaction-value of the three methyl-groups for the velocity is — 78. Thus each methyl-group has a value of — 26 in tertiary alcohols, the value is — 20.8 in secondary alcohols, and in primary it is — 12.6. Thus the substitution of the three atoms of hydrogen in methyl alcohol almost destroys the power of forming ethers.

The author regards phenols as tertiary alcohols, and the following table contains the etherification data of several phenols expressed in terms of methyl alcohol:—

	Velocity.	Limit.
Phenol, $(\text{C}_6\text{H}_5)\text{C.HO}$	2.0	12.4
Paracresol, $(\text{C}_6\text{H}_4\text{Me})\text{C.HO}$	3.7	13.7
Thymol, $(\text{C}_6\text{H}_3\text{Me.C}_3\text{H}_7)\text{C.HO}$..	1.4	13.6
α -Naphthol, $(\text{C}_{10}\text{H}_7)\text{C.HO}$?	8.8

Thus it is seen that the substitution in methyl alcohol of three atoms by a single radicle (C_6H_5) has a very marked influence on the velocity, which is attributed to the relatively small amount of hydrogen present in the radicle.

Dihydric Alcohols.—By a similar comparison of the etherification data of glycols with those of methyl alcohol, it is shown that the substitution in a monohydric alcohol of a hydroxyl group decreases the limit and velocity of etherification, and that the amount of this differ-

ence is greater when by this substitution a secondary alcohol group is formed than when a primary alcohol group is formed.

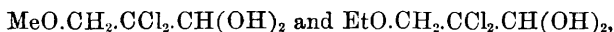
Polyhydric Alcohols.—The following etherification data of several polyhydric alcohols, compared with those of methyl alcohol, show that both the limit and the velocity decrease with increase in molecular weight, which is probably to be attributed to the substitution in methyl alcohols of groups containing more and more oxygen.

	Velocity.	Limit.
Methyl alcohol, HCH_2OH	80.0	100.0
Glycol, $(\text{CH}_2\text{OH})\text{CH}_2\text{OH}$	61.7	77.4
Glycerol, $[\text{CH}_2\text{OH}(\text{CHOH})]\text{CH}_2\text{OH}$	52.2	66.2
Erythrol, $[\text{CH}_2\text{OH}(\text{CH.OH})_2]\text{CH}_2\text{OH}$	34.0	57.6
Mannitol, $[\text{CH}_2\text{OH}(\text{CH.OH})_4]\text{CH}_2\text{OH}$	29.6	38.0

P. P. B.

Action of Hypochlorous Acid on Propargylic Compounds.

By L. HENRY (*Compt. rend.*, **93**, 388—390).—The author had hoped by the fixation of hypochlorous acid on the propargylic compounds to be able to produce an isocrotylic alcohol, $\text{Me}_2\text{C}:\text{CHOH}$, but the experiment was unsuccessful. Methyl and ethyl propargylic ethers react readily with hypochlorous acid to form thick oils, which cannot be distilled under ordinary pressure without decomposition. It was found that 2 equivalents of hypochlorous acid were taken up to form compounds probably of the following constitution—



but the author has not succeeded in converting the compounds into their corresponding acids by oxidation.

The probability of the formation of either aldehydes or ketones by the direct combination of acetylene derivatives with hypochlorous anhydride is also discussed; acetylene itself will doubtless form dichloraldehyde, $\text{CH}:\text{CH} + \text{Cl}_2\text{O} = \text{CHCl}_2.\text{CHO}$. V. H. V.

Absorption of Moisture by Glycerol. By E. WILLIAMS (*Chem. Centr.*, 1881, 76).—The author placed 100 grams glycerol (sp. gr. 1.25) in vessels of different diameters, and found the increase in weight in four months to vary from 4.1 grams to 58.5 grams.

F. L. T.

Dichlorhydrin and its Oxidation-products. By W. MARKOWNIKOFF (*Annalen*, **208**, 349—363).—*Dichlorhydrin* prepared by the action of aqueous hydrochloric acid on epichlorhydrin (b. p. 170—180°), and purified by repeated redistillation, is an oily liquid of sp. gr. 1.383 at 0° and 1.367 at 19°. It dissolves in nine parts of water at 19°, and in six parts at 72°. Under a pressure of 765 mm. the liquid boils at 171—171.5° (corr. 175.8—176.3°). Crude dichlorhydrin is evidently a mixture of at least two bodies. Hübner and Müller (*Zeits. Chem.*, 1870, 343; *Annalen*, **159**, 168) pointed out that the crude compound had not a fixed boiling point, and attributed this to the presence of two isomeric dichlorhydrins. The author, however, finds that the variation in the boiling point is due to the presence of acetochlorhydrin, and not to an isomeride of dichlorhydrin.

On oxidation with potassium chromate and dilute sulphuric acid, dichlorhydrin yields *dichloracetone*, $\text{ClH}_2\text{C.CO.CH}_2\text{Cl}$, which is isomeric with the dichloracetone prepared by the action of chlorine on acetone. The dichloracetone from dichlorhydrin crystallises in transparent rhombic plates (m. p. 45°), which are soluble in alcohol, ether, and water. It boils at 167.5° , but is volatile at the ordinary temperatures; the vapour irritates the mucous membrane, and also attacks the epidermis. With acid sodium sulphite, this substance forms a compound, $\text{C}_3\text{H}_4\text{Cl}_2\text{O.SO}_3\text{NaH} + 2\frac{1}{2}\text{H}_2\text{O}$, which crystallises in efflorescent quadratic prisms. The dichloracetone described by Glutz and Fischer was an impure preparation, probably containing dichlorhydrin.

W. C. W.

Pyruvic Alcohol and its Derivatives. By L. HENRY (*Compt. rend.*, **93**, 421—422).—The hydration of the propargyl compounds and their conversion into derivatives of pyruvic alcohol are interesting as a completion of the relations which exist between them and the derivatives of acetone. The author has already shown that pyruvic acetate is produced by the action of potassium acetate on monochloracetone, but he was unable to convert the ethereal salt into the alcohol. On heating propargylic ether with water in presence of mercuric bromide (Kutscheroff's reaction) it is converted into ethyl pyruvyl ether, $\text{COMe.CH}_2\text{OEt}$, a colourless liquid (b. p. 128° ; sp. gr. = 92) of peculiar fresh odour and burning taste; it is isomeric with ethyl propionate. By an analogous reaction, propargylic acetate is converted by water into pyruvic acetate. All the pyruvic compounds act as powerful reducing agents. The author considers it probable that dipropargyl on hydration would furnish a hexylic diacetone of the composition, $\text{COMe.}(\text{CH}_2)_2\text{COMe}$.

V. H. V.

A Sugar present in the Grain of Soja Hispidia. By A. LEVALLOIS (*Compt. rend.*, **93**, 281).—The author has studied the properties of this sugar, the presence of which he has indicated (*Abstr.*, 1880, 796). Precipitated from its alcoholic solution by ether and dried in a vacuum, it furnishes a very deliquescent mass; it does not reduce Fehling's solution, and is converted into glucose by mineral acids. It has a dextrorotatory power of about $+115^\circ$; after inversion this value becomes $+35^\circ$. It is quickly fermented by yeast, and when warmed with nitric acid it gives mucic and oxalic acids. It seems that this substance is a distinct sugar; in some of its properties it resembles cane-sugar, but in the formation of mucic acid it is more analogous to mellitose.

V. H. V.

Bast Fibres. By E. T. BEVAN and C. F. CROSS (*Chem. News*, **44**, 64).—Bast fibres when fused with potassium hydroxide yield considerable quantities of protocathechuic acid, together with small quantities of phloroglucinol. This fact confirms the authors' supposition that the aromatic constituents of bast fibres are identical with the tannin group. When Esparto "resin" is treated with sulphuric acid, it yields products resembling those obtained from digallic acid under the same conditions. When bast fibre is triturated with sulphuric acid, it dissolves to a viscous purple solution, and when this is heated for a short time at $80\text{--}90^\circ$ and poured into water, the fibre substance

is precipitated as a black spongy mass, which when treated with chlorine in presence of water, yields an orange-coloured substance completely soluble in alcohol and alkalis, and closely resembling the aromatic chloro-derivatives previously described. When bleached cotton is dissolved in strong acid and heated to 80—90°, the liquid effervesces and gives off acetic acid, and in a short time swells up, forming a voluminous black mass, which, when purified by treatment with water, contains 59 per cent. carbon and 5.4 per cent. hydrogen. When treated with potassium chlorate and hydrochloric acid, it is converted into a bright orange-coloured substance, soluble in alcohol and alkalis, similar in composition ($n\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{O}_{10}$) and properties to the chloro-derivatives previously mentioned. When the black substance is treated with nitric acid of sp. gr. 1.4 at 30°, it yields a red solution, which deposits a flocculent yellow nitro-compound on dilution. From these experiments, it follows that the black substances produced by the action of sulphuric acid on carbohydrates below 100° are not in any special sense more carbonaceous than is ordinary alcohol. Since by this action cellulose is so modified as to resemble the compound obtained from liquefied fibres, *lignin* may be regarded as derived from cellulose by a simple change, possibly dehydration. The study of these compounds may be expected to throw light on the relations between the carbohydrates and aromatic compounds, and also on the origin of coal.

C. H. B.

Action of Methylamine on Epichlorhydrin. By E. REBOUL (*Compt. rend.*, **93**, 423—425).—It is probable that epichlorhydrin should react with methylamine to form an oxygenated tetrammonium

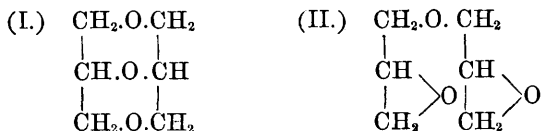
chloride of formula $\text{CINEt}_3\text{CH}_2\text{CH} \begin{array}{c} \text{O} \\ \diagup \quad | \\ \text{CH}_2 \end{array}$, or oxallyl-methyl-ammonium chloride.

When epichlorhydrin and methylamine in equal volumes are heated in sealed tubes at 100°, a yellowish oily layer separates out, which increases gradually. This thick syrup exhibits no signs of crystallisation when cooled to -20°, or when evaporated in a vacuum over sulphuric acid, it is *oxallyltriethylammonium* chloride. The *platino-chloride* crystallises from absolute alcohol in yellowish-orange needles. When the chloride in aqueous solution is decomposed by silver oxide, an alkaline liquid is obtained, which on evaporation gives a thick uncrystallisable syrup, possessing properties analogous to the tetraalcoholic ammonium hydrates. The *sulphate* and *nitrate* form very deliquescent crystals, very soluble in absolute alcohol.

V. H. V.

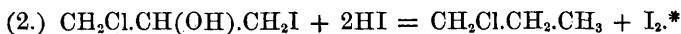
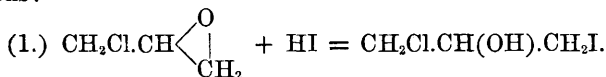
Glyceric Ether. By R. D. SILVA (*Compt. rend.*, **93**, 418—421).—In the preparation of allyl alcohol from glycerol, a considerable quantity of a black residue is formed, from which Gegerfelt has separated a liquid of composition $\text{C}_6\text{H}_{10}\text{O}_3$, and the so-called glyceric ether. The author has further examined this residue, and has obtained a principal fraction boiling at 169—171°, and a subsidiary portion boiling from 185—190°, of which the former is the glyceric ether of Gegerfelt. This compound is a thick, colourless, inflammable liquid (b. p. 169—

171°), soluble in water, alcohol, and ether; sp. gr. at 0° = 1.1453. Inasmuch as this compound exhibits none of the characteristic reactions of the ethers, Gegerfelt considers that of the following possible structural formulæ, the second is the more probable.



The author, however, inclines to the first formula, and if this view is correct, the action of hydriodic acid would convert the compound into glycerol and tri-iodopropane, $\text{CH}_2\text{I}.\text{CHI}.\text{CH}_2\text{I}$, which, by the continued action of hydriodic acid should yield isopropyl iodide. This was confirmed by experiment (this Journal, 1876 [i], 60).

On passing hydriodic acid into epichlorhydrin, the liquid thickens, iodine separates out, and a volatile liquid distils over. This liquid is normal propyl chloride, produced by the following series of reactions:—



This offers an easy method for the conversion of glycerol into normal propyl alcohol.

V. H. V.

Preparation of Formic Aldehyde. By A. MICHAEL (*Am. Chem. J.*, **1**, 418—420).—Hofmann's method of preparing this compound by slow oxidation of methyl alcohol yields a dilute solution of the aldehyde in methyl alcohol. An aqueous solution containing 16 to 18 per cent. of the aldehyde may be prepared by heating methylic monochloracetate with water, the reaction taking place as represented by the equation,



100 g. methylic chloracetate and 55 g. distilled water are heated for 30 minutes to an hour at 100° in a strong closed flask; and the contents are then neutralised with strong caustic soda, and distilled in an oil-bath, whereby a colourless, usually slightly acid liquid is obtained, which may be purified by neutralisation and redistillation; 110 g. methyl chloracetate generally yields 140—145 g. of aqueous solution, containing 16—18 per cent. methyl chloracetate.

The aqueous solution of the aldehyde, evaporated in a vacuum to about a third of its original bulk, deposits the polymeric compound *trioxymethylene*, $\text{C}_3\text{H}_6\text{O}_3$; and if the evaporation be stopped just before this separation begins, a concentrated solution is obtained, containing about 40 per cent. of the aldehyde.

H. W.

* This last equation is wrong (also in the original paper); it should perhaps be:

$$\text{CH}_2\text{Cl}.\text{CHOH}.\text{CH}_2\text{I} + 3\text{HI} = \text{CH}_2\text{Cl}.\text{CH}_2.\text{CH}_3 + \text{H}_2\text{O} + 2\text{I}_2. \quad [\text{Ed.}]$$

Some New Uranium Salts. By F. W. CLARKE and MARY OWENS (*Amer. Chem. J.*, **2**, 331).—Sodium uranate dissolves readily in the substituted acetic acids, yielding definite salts analogous to the well-known sodio-uranic acetate.

Sodio-uranic monochloracetate, $\text{Na}(\text{U}_2\text{O}_2) \cdot (\text{C}_2\text{H}_2\text{ClO}_2)_3 + 2\text{H}_2\text{O}$, forms large sulphur-yellow crystals of sp. gr. 2.748 at 14°. The *dichloracetate* $\text{Na}(\text{U}_2\text{O}_2)(\text{C}_2\text{HCl}_2\text{O}_2)_3$ and the monobromacetate $\text{Na}(\text{U}_2\text{O}_2)(\text{C}_2\text{H}_2\text{BrO}_2)_3$ are anhydrous, and form small yellow crystals, those of the latter being clustered in regular stellate groups. A solution of the double trichloracetate dried up to a gummy mass. H. W.

Substituted Acrylic Acids from Bromopropiolic Acid. By H. HILL and C. F. MABERY (*Am. Chem. J.*, **3**, 172—184).—1. *Dibromacrylic Acid of Fittig and Petri*.—The solution of bromopropiolic acid in strong hydrobromic acid (b. p. 126°) deposits, after a short time, crystals of a dibromacrylic acid identical with that which Fittig and Petri obtained by the decomposition of tribromosuccinic acid. The same acid may also be advantageously prepared from the solution of the propiolate and bromide obtained in the preparation of barium dibromacrylate by the action of baryta-water on mucobromic acid: the barium may be precipitated by dilute sulphuric acid, the filtrate concentrated on the water-bath, and the acid which separates on cooling purified by recrystallisation. From a hot concentrated solution, it separates at first as an oil, but after cooling to a certain extent, it is deposited in pearly scales melting at 85—86°. Its aqueous solution, saturated at 20°, contains 2.91 to 3.16 per cent. of the acid. Fittig and Petri found 3.355. The *barium salt* obtained by neutralisation crystallises in rectangular plates, having in the air-dried state the composition $(\text{C}_3\text{HBr}_2\text{O}_2)_2\text{Ba} + 2\text{H}_2\text{O}$, the water being given off at 100°. The *calcium salt*, $(\text{C}_3\text{HBr}_2\text{O}_2)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$ crystallises in long radiate needles.

2. *Iodobromacrylic acid*, $\text{C}_3\text{H}_2\text{BrIO}_2$, is easily prepared by dissolving bromopropiolic acid in concentrated hydriodic acid (b. p. 127°), and separates from a hot concentrated aqueous solution as an oil, but at a lower temperature in pearly scales which melt at 110°. It dissolves readily in alcohol, ether, or chloroform, sparingly in benzene, carbon bisulphide, and light petroleum. An aqueous solution saturated at 20° contains 1.70 per cent. of the acid. The *barium salt*, $(\text{C}_3\text{HBrIO}_2)_2\text{Ba} + 3\text{H}_2\text{O}$, crystallises from strong solutions in slender needles, from more dilute solutions in rectangular plates. In the air-dried state, it contains 3 mols. water, which it loses in a vacuum over sulphuric acid. Its solution saturated at 20°, contains 13.88 per cent. of the anhydrous salt. The *calcium salt*, $(\text{C}_3\text{HBrIO}_2)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$, closely resembles the barium salt in appearance, but is more soluble in water. It loses its crystal-water completely in a vacuum over sulphuric acid, or when heated to 80°. The *silver salt*, $\text{C}_3\text{HBrIO}_2\text{Ag}$, obtained by precipitation, forms short clustered needles, which may be recrystallised from water with but slight decomposition.

Chlorobromacrylic acid is formed by direct combination of bromopropiolic acid with hydrochloric acid, but the action is much slower than with hydriodic acid.

3. *Tribromacrylic acid*, $C_3HBr_3O_2$, is produced by slowly adding an excess of bromine to an aqueous solution of bromopropiolic acid, and separates partly as an oil, which gradually solidifies, whilst the remainder may be extracted from the aqueous solution by ether. The solid product, after being freed from liquid by pressure, and recrystallised from chloroform, or better from benzene, crystallises in colourless oblique prisms, very soluble in ether and in alcohol, less soluble in cold, readily in hot chloroform or benzene, soluble also in carbon bisulphide and in light petroleum, only sparingly soluble in water even at the boiling heat. Melts at 118° . A solution saturated at 20° contains 1.33—1.38 per cent. of the acid. It is scarcely affected by boiling with excess of barium hydroxide, but is slowly decomposed by boiling with alcoholic potash. The *barium salt*, $(C_3Br_3O_2)Ba + 3H_2O$, prepared by neutralisation, crystallises from a concentrated solution on cooling, in long needles which effloresce over sulphuric acid. Its aqueous solution saturated at 20° contains 23.62—23.69 per cent. of the anhydrous salt. The *calcium salt*, $(C_3Br_3O_2)_2Ca + H_2O$, crystallises in needles which are permanent in the air, but lose weight over sulphuric acid. The *silver salt*, $C_3Br_3O_2Ag$, is tolerably stable and crystallises in six-sided plates.

H. W.

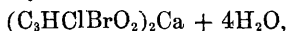
Di-iodobromacrylic and Chlorobromacrylic Acids. By C. F. MABERY and RACHAEL LLOYD (*Amer. Chem. J.*, **3**, 124—129).—Di-iodobromacrylic acid, $C_3I_2BrHO_2$, is formed when bromopropiolic acid, C_3HBrO_2 (this Journal, 1879, Abstr., 225), is left for some time in contact with an ethereal solution of iodine, more quickly however by heating bromopropiolic acid with a little more than the calculated weight of iodine and five parts by weight of ether, for two hours on the water-bath with a reflux condenser. On allowing the ether to evaporate, extracting the residue with successive portions of warm water, and concentrating by evaporation, the di-iodobromacrylic acid is deposited on cooling in glistening plates, which may be purified by recrystallisation from hot water. By evaporation, the mother-liquors give an oily product, which solidifies on standing, but is difficult to purify.

Di-iodobromacrylic acid crystallises in flat white six-sided plates, very slightly soluble in cold water, readily in hot water, very soluble in ether, alcohol, carbon bisulphide, and light petroleum. It melts at 160° , and sublimes slowly at higher temperatures, apparently unchanged. It dissolves in 48.37 parts of water at 20° .

Barium di-iodobromacrylate, $Ba(C_3I_2BrO_2)_2 + 4H_2O$, prepared by saturation, crystallises in stellate groups of flat prisms, very soluble in cold, less soluble in hot water. The *calcium salt*, $Ca(C_3I_2BrO_2)_2$, crystallises in branching needles very soluble in water. The *silver salt*, $AgC_3I_2BrO_2$, prepared by precipitation, is very slightly soluble in cold water, but dissolves readily in dilute nitric acid, and crystallises in oblique prisms. The *potassium salt*, $C_3I_2BrO_2K + 2H_2O$, crystallises in oblique prisms, very soluble in water.

Chlorobromacrylic acid, $C_3H_2ClBrO_2$, may be prepared by treating bromopropiolic with ordinary fuming hydrochloric acid; more readily however by the action of hydrochloric acid saturated at 0° .

The acid liquid soon becomes filled with crystals of the chlorobrominated acid, the reaction being complete in about 24 hours; and the product, after being freed from excess of hydrochloric acid by decantation and pressure between filter-paper, may be further purified by crystallisation from hot water. It separates from a hot solution as an oily liquid, but crystallises when nearly cold in elongated flat prisms or needles. It melts at 70° , and sublimes freely at a somewhat higher temperature; it dissolves much more readily in hot than in cold water, easily in ether, alcohol, benzene, and carbon bisulphide. The *barium salt*, $(C_3HClBrO_2)_2Ba + 2H_2O$, crystallises in flattened prisms, apparently monoclinic. The *calcium salt*,



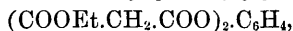
forms branching needles, very soluble in hot, less soluble in cold water. The *silver salt*, $C_3HAgClBrO_2$, prepared by adding silver nitrate and ammonia to a solution of the acid, forms microscopic needles almost insoluble in cold water. The *potassium salt*, $C_3HKClBrO_2$, forms irregular pointed prisms, less soluble in cold than in hot water.

Chlorobromacrylic acid dissolved in chloroform and left in contact for several days with rather more than 1 mol. bromine, is converted into chlorotribromopropionic acid, $C_3H_2ClBr_3O_2$, which separates in large prismatic crystals, melting after recrystallisation from carbon bisulphide, at about 98° .
H. W.

Methylcrotonic and Angelic Acids. By E. SCHMIDT (*Annalen*, **208**, 249—268).—It has been previously pointed out by the author (*Ber.*, **12**, 252; and this Journal, 1879, Abstracts, 617) that the valeric acid formed by the action of zinc and weak sulphuric acid on dilute alcoholic solutions of hydriodomethylcrotonic acid (m. p. 86.5°) and hydriodangelic acid (m. p. 46°) is identical with methylethylacetic acid. The identity of these acids was established by a comparison of the sp. gr. (0.940 at 17°) and boiling point of the acids (173 — 175° not corr.) and by an examination of the following salts:— $C_5H_9AgO_2$, feather-shaped crystals, soluble in hot water; $Ba(C_5H_9O_2)_2$, transparent amorphous mass, resembling varnish, in which slender, needle-shaped crystals are occasionally found; $Ca(C_5H_9O_2)_2 + 5H_2O$, colourless, efflorescent needles, soluble in water; $(C_5H_9O_2)_2Cu$, bluish-green crystalline precipitate. The zinc salt forms silky white needles, which are more soluble in cold than in hot water. The manganese salt is amorphous. The rest of the paper has already appeared in the *Berichte* (*loc. cit.*).
W. C. W.

Calcium Double Salt of Methylcrotonic and Isobutylformic Acids. By E. SCHMIDT (*Annalen*, **208**, 268—279).—The existence of the double salt, $(C_5H_7O_2)_2Ca.(C_5H_9O_2)_2Ca + 9H_2O$, discovered by the author in conjunction with Berendes (*Annalen*, **191**, 105), has been recently called in question by Conrad and Bischoff, who declare that this compound is merely calcium methylethylacetate. The author has therefore again prepared this double salt from methylcrotonic and isobutylformic acids, and has satisfied himself that it is not calcium methylethylacetate. It crystallises in colourless needles, which are frequently more than an inch in length.
W. C. W.

Substituted Glycollic Acids. By M. SENFF (*Annalen*, **208**, 270—277).—*Ethyl propionylglycollate*, $\text{COOEt} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_3\text{H}_5\text{O}$, prepared by heating a mixture of ethyl monochloracetate and anhydrous sodium propionate at 175° for 30 hours, is a colourless, highly refractive liquid (sp. gr. 1.0052 at 22° , b. p. 201°). It is soluble in hot water. *Ethyl butyrylglycollate* has a sp. gr. of 1.0288 at 22.5° . *Ethyl isobutyrylglycollate* boils at 195° , and has a sp. gr. of 1.0240 at 22.5° . *Ethyl benzo-glycollate* is easily obtained by heating a mixture of sodium benzoate and ethyl monochloracetate at 180° . It cannot be distilled even in a vacuum without undergoing decomposition. *Ethyl salicylglycollate*, $\text{COOEt} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C} \cdot \text{C}_7\text{H}_5\text{O}_2$, and *ethyl phthalylglycollate*,



resemble the preceding compound in their properties and mode of preparation. Attempts to isolate the acids contained in the ethyl salts of propionyl, butyryl, isobutyryl, benzoyl, salicyl, and phthalyl glycolic acids were unsuccessful.

W. C. W.

Tetrylenedicarboxylic Acid (Homoitaconic Acid). By W. MARKOWNIKOFF and A. KRESTOWNIKOFF (*Annalen*, **208**, 333—349).—In a preliminary notice (*Ber.*, **12**, 1489, and this Journal, Abstr., 1880, 238), the authors pointed out that a mixture of alcohol, ethylic ethylacetate, ethyllactic acid, and ethyl homoitaconate, is produced by the action of dry sodium ethylate on ethyl α -chloropropionate at 80° . An analogous reaction takes place when dry sodium methylate is added to warm ethyl or methyl chloropropionate. In the latter case, the methyl salt of methyllactic acid (b. p. 135 — 138°) is formed as a by-product.

Tetrylenedicarboxylic or *homoitaconic acid* is deposited when the ethyl salt is heated for two or three days with an excess of strong hydrochloric acid. It is purified by recrystallisation from water and treatment with animal charcoal, or by conversion into its lead salt. The pure acid crystallises in rhombic prisms, soluble in hot water and alcohol. It melts at 170° , and sublimes at a higher temperature, forming needle-shaped crystals. The calcium, zinc, and sodium salts are soluble in water, and uncrystallisable. $\text{PbC}_6\text{H}_8\text{O}_4 + \frac{1}{2}\text{H}_2\text{O}$ is deposited in microscopic needles, when a dilute solution of the acid is neutralised with lead carbonate. $\text{Ag}_2\text{C}_6\text{H}_8\text{O}_4$ is amorphous, and insoluble in water. Ethyl homoitaconate is a viscid, colourless liquid, b. p. 230° , and the methyl salt boils at 220° .

The acid dissolves in hydrobromic and hydriodic acids without undergoing any change. It does not unite with bromine to form addition products; neither does it yield an anhydride when heated at 290° .

The chief products of the action of sodium ethylate on ethyl chloracetate is ethylic ethylglycollate, but by the action of sodium ethylate on ethyl bromobutyrate, a mixture of ethylic ethoxybutyrate, ethoxybutyric acid, and an ethereal salt (b. p. 245 — 253°) is formed. On saponification with strong hydrochloric acid, the ethereal compound appears to yield two isomeric acids of the composition $\text{C}_8\text{H}_{12}\text{O}_4$.

W. C. W.

A New Formation of Ethylthiocarbimide. By A. MICHAEL (*Am. Chem. J.*, **1**, 416—418).—Hofmann and V. Meyer have shown that the product obtained by the action of ethyl iodide on silver thiocyanate consists wholly of normal ethyl thiocyanate without a trace of the isocyanate or thiocarbimide. This seems to show that silver thiocyanate is itself a normal thiocyanate, that is to say, that its silver-atom is directly attached to the sulphur, and not to the nitrogen-atom, in consequence, we may suppose, of silver having a stronger affinity for sulphur than for nitrogen. Accordingly it seemed probable that by employing a thiocyanate containing a metal, such as mercury, whose affinity for sulphur is less than that of silver, while its affinity for nitrogen is greater, it might be possible to obtain an isothiocyanate, or thiocarbimide. This reaction has indeed already been tried by Schlagdenhauffen (*Ann. Chim. Phys.* [3], **56**, 297), who thereby obtained normal ethyl thiocyanate, together with a red mass, which he did not further examine. Michael finds that ethyl iodide acts on mercuric thiocyanate, even at 100°, but more readily on heating the materials together in a sealed tube at 146—150°. On opening the tube after heating for about 2½ hours, a strong smell of ethylthiocarbimide was observed, and a dark-red sediment had formed; and on distilling the contents of the tube in a current of steam, an oil passed over, which, when dried by calcium chloride and redistilled, yielded a small quantity of oil, passing over below 135°, the presence of ethylthiocarbimide in which was indicated by its pungent odour, and further demonstrated by treating it with aniline, whereby it was converted into ethylphenylthiocarbimide: $\text{N}(\text{CS})\text{Et} + \text{NPhH}_2 = \text{N}_2(\text{CS})\text{EtPhH}_2$. The quantity of ethylthiocarbimide formed in this reaction does not exceed 3 per cent. of the normal ethyl thiocyanate, and even this is but small. The chief product of the reaction is in fact the red mass mentioned by Schlagdenhauffen, which is possibly a compound of ethylthiocarbimide with mercuric iodide; it contains Hg, C, S, and I, and on distillation yields a heavy oil containing sulphur.

Methyl and amyl iodides act on mercuric iodide in a similar manner, forming liquids which have the strong penetrating odour of allylthiocarbimides or mustard oils.
H. W.

Certain Volatile Products in Crude Coal-tar Benzenes. By WATSON SMITH (*Chem. News*, **44**, 138—140).—Crude benzenes (so called "aniline benzenes") contain small quantities of amylenes, together with carbon bisulphide, to the extent, in the sample examined, of 5.92 per cent. by volume. The carbon bisulphide is probably due to the action of a high temperature in the retorts on coals containing much sulphur. Only minute traces of alcohol could be detected, and acetonitril was not present. The author considers that the ethyl alcohol found by Vincent and Delachanal (*Compt. rend.*, **86**, 340), and by Witt (*Ber.*, 1877, 2227) in rectified benzene, was a product of the action of the sulphuric acid used in the rectification on ethylene dissolved in the oils.
C. H. B.

Petrocene, a Product of the Destructive Distillation of Petroleum. By S. P. SADTLER and H. G. McCARTER (*Am. Chem. J.*, **1**, 30—32).—The name "petrocene" was given by Hemilian (*Ber.*, **9**,

1604; this Journal, 1877, 2, 866) to a solid hydrocarbon (m. p. above 300°) obtained from the highest-boiling portion of American petroleum. A similar substance was examined in 1878 by Prunier and David (*Compt. rend.*, 87, 991; this Journal, 1879, Abstr., 309), who found it to contain from 88 to 96 per cent. carbon, and regarded it as a mixture of anthracene, phenanthrene, chrysene, chrysogen, and other hydrocarbons.

The authors of the present paper find that the hydrocarbons of which this residue is composed cannot well be separated by treatment with solvents; but by combining them with picric acid, and fractional crystallisation of the products from alcohol and benzene, they obtained three distinct crystallisations, two of red crystals, and one of brown plates. These were carefully picked apart and purified by recrystallisation, and when decomposed by ammonia, yielded two well-marked hydrocarbons, one melting at 280° , the other at 178° . The composition of these hydrocarbons has not yet been exactly made out; but by converting them into quinones, and these into the corresponding dihydroxyquinones (alizarins), and analysing these products, results were obtained which render it probable that the hydrocarbon melting at 280° has the composition of a *dimethylantracene*, $C_{16}H_{14}$, although it does not agree in its properties with either of the known dimethylantracenes. The hydrocarbon melting at 178° appears to have the composition of a *monomethylantracene*. Both these hydrocarbons were undoubtedly contaminated with chrysene, or some similar compound having a higher percentage of carbon, from which it is extremely difficult to free them.

H. W.

Compounds of Aromatic Amines with Silver Nitrate and Sulphate. By W. G. MIXTER (*Am. Chem. J.*, 1, 239—243).—A compound of 2 mols. melaniline with 1 mol. silver nitrate was obtained by Hofmann in 1848 (*Annalen*, 67, 129), and Griess in 1862 (*ibid.*, 121, 257) obtained compounds of silver nitrate with azodiphenyldiamine and azobromodiphenyldiamine, having the formulæ $C_{12}H_{11}N_3, AgNO_3$ and $C_{12}H_9Br_2N_3, AgNO_3$. The author has already prepared compounds of silver nitrate with amyridenamine (this Journal, 1878, Abstr., 564), and of silver sulphate with ethyridenamine (*ibid.*, 1880, 234), and he has lately obtained the following compounds of silver nitrate and sulphate with aromatic monamines.

Aniline with Silver sulphate, $(C_6H_7N)_4Ag_2(SO_4)_2 \cdot 2H_2O$.—This compound was prepared by dissolving 5 grams silver sulphate and 6 grams aniline in boiling water. Some silver was reduced, and a dark residue was left. On cooling, the filtrate from the hot liquid gave a mass of hair-like rose-tinted crystals, the colour being probably due to the mother-liquor. The compound left in a vacuum over oil of vitriol for two days, lost 33.08 per cent.; 2 mols. each of aniline and water are equal to 30.83 per cent. Absolute alcohol removes the greater part of the aniline.

Paratoluidine with Silver sulphate, $(C_6H_8N)_4Ag_2SO_4 \cdot 2H_2O$.—Prepared in like manner with 6 g. of toluidine and 4.5 g. silver sulphate. It resembles the preceding compound in appearance, and is decomposed by absolute alcohol, which removes the whole of the toluidine.

Metanitraniline with Silver nitrate, $[C_6H_5(NO_2)N]_4AgNO_3$.—Prepared by adding 13 g. metanitraniline (m. p. 116°) dissolved in boiling absolute alcohol to a boiling solution of 2 g. silver nitrate in absolute alcohol, and separates on cooling in a mass of hair-like yellow crystals, melting at 124 – 125° . Cold water completely removes the silver nitrate, leaving *m*-nitraniline.

Nitrotoluidine with Silver nitrate, $[C_7H_7(NO_2)N]AgNO_3$.—Prepared by adding 2.5 g. silver nitrate to 8 g. nitrotoluidine (m. p. 77.5°) dissolved in boiling water. It is a greenish-yellow crystalline body, which dissolves in absolute alcohol, and melts without decomposition at 131 – 132° . It is not affected by light. Equal weights of silver nitrate and nitrotoluidine give the same compound.

Paratoluidine with Silver nitrate, $(C_7H_7N)_2AgNO_3$.—Prepared by adding a hot aqueous solution of *p*-toluidine, with agitation, to a cold solution of silver nitrate. It is a white crystalline body which melts with decomposition at 101° , and is slowly decomposed by absolute alcohol, with separation of a brownish mass. H. W.

Anhydro-compounds. By H. HÜBNER (*Annalen*, 208, 278–332).—Many of the facts of this paper have appeared in the form of short communications to the *Berichte* (6, 798 and 1128; 7, 463 and 1314; 8, 875 and 562; 9, 774 and 775; 10, 1708, 1710, 1716) and this Journal (1874, 78; 1876, ii, 309; 1878, Abstr., 142–144).

A mixture of ortho- and para-nitrobenzanilides is formed by gradually adding 10 grams of benzanilide (m. p. 163°) to 100 grams of nitric acid (sp. gr. 1.45), cooled down to 5° . The solution is poured into 10 times its volume of cold water, and the precipitated nitranilides are washed with water and dried. By treatment with cold benzene, the orthonitranilide dissolves, leaving the parabenznitranilide undissolved. The substances are purified by recrystallisation from alcohol.

By boiling *paranitrobenzanilide*, $C_6H_4(NO_2).NH.COPh$ [4 : 1], with a dilute solution of an alkali, *paranitraniline* (m. p. 146°) is obtained. On reduction with tin and hydrochloric acid, *paranitrobenzanilide* yields *paramidobenzanilide*, $C_6H_4(NH_2).NH.COPh$ [4 : 1], which crystallises in colourless plates (m. p. 128°), freely soluble in alcohol and in chloroform. The hydrochloride and sulphate of this base crystallise in needles, which are sparingly soluble in cold water. *Paramidobenzene*, obtained by boiling *paramidobenzanilide* with dilute potassium hydroxide, crystallises in colourless plates (m. p. 140°), soluble in alcohol and ether. The hydrochloride also crystallises in plates. It is very soluble in water.

The separation of *metanitrobenzanilide* from its isomerides is described in *Ber.*, 9, 774. On treatment with dilute alkalis, it yields *metanitraniline*, which crystallises in yellow needles (m. p. 112°), soluble in alcohol. The nitranilines are best prepared by slowly dropping a solution of aniline sulphate in sulphuric acid into a well cooled mixture of strong nitric and sulphuric acids. The product is slowly poured into cold water, and the acid solution neutralised with sodium hydroxide, which causes the nitranilines to separate out. On distillation in a current of steam, orthonitraniline is carried over, the

para- and *meta*-derivatives remaining in the retort. These two compounds are easily separated by recrystallisation from benzene or water. Pure orthonitraniline melts at 71° , the *meta*-compound at 114° , and *para*-nitraniline at 155° .

When *orthonitrobenzanilide* (m. p. 94°) is boiled with a strong solution of potassium hydroxide, *orthonitrophenol* and *orthonitraniline* are formed. The latter compound on reduction yields *orthodiamidobenzene* (m. p. 120°).

Anhydrobenzoyldiamidobenzene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CPh}$, is prepared by

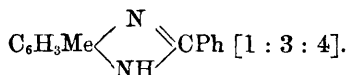
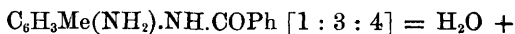
heating a mixture of *orthonitrobenzanilide* and finely granulated metallic tin (1 mol. : 3 atoms), made into a paste with strong hydrochloric acid. When the anilide is completely dissolved, the liquid is decanted from the undissolved tin and evaporated to dryness on a water-bath. The residue is stirred up with strong ammonia, and warmed with yellow ammonium sulphide until the whole of the tin is dissolved. The anhydro-base which remains undissolved is washed with water. From its solution in glacial acetic acid, the base is deposited in plates (m. p. 250°), soluble in alcohol. The salts of this base crystallise in needles; and with the exception of the hydrochloride, $\text{C}_{13}\text{H}_{10}\text{N}_2\text{HCl}$, they are only sparingly soluble in cold water.

Nitro-anhydrobenzoyldiamidobenzene, $\text{C}_6\text{H}_3(\text{NO}_2) \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CPh}$ (m. p.

196°), has feeble basic properties. On reduction, it yields the *amido*-compound, which crystallises in small needles (m. p. 240°), soluble in alcohol, but insoluble in water. This base forms the following salts: $\text{C}_{10}\text{H}_{11}\text{N}_3 \cdot \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$, colourless needles, sparingly soluble in hot water; $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl}$, colourless plates, freely soluble in water, and $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HNO}_3$, colourless plates, which dissolve readily in water.

Anhydro-compounds from Paratoluidine.—The formation of *meta*-nitrobenzoparatoluide (m. p. 143°), *dinitrobenzoparatoluide* (m. p. 186°), and *metanitroparatoluidine* (m. p. 114°), from *benzoparatoluide* (m. p. 155°), has been already described by Kelbe (*Ber.*, **8**, 875).

Metamidobenzoparatoluide (m. p. 192°), obtained by the reduction of *metanitrobenzoparatoluide* with tin and hydrochloric acid, is soluble in alcohol and chloroform. It is deprived of a molecule of water by the action of benzoic chloride, and an anhydro-base (m. p. 239°) is formed—



This base is soluble in hot alcohol, ether, chloroform, and glacial acetic acid. The *hydrochloride* and *nitrate* form colourless needles, soluble in boiling water and in hot alcohol. The *sulphate* also crystallises in needles, which are sparingly soluble in alcohol and in hot water.

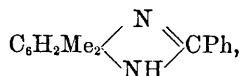
When dinitrobenzoparatoluide is treated with sulphuretted hydrogen, it yields *amidonitrobenzoparatoluide*—



crystallising in red needles (m. p. 138°), and on reduction with tin and hydrochloric acid the dinitro-compound yields *diamidobenzoparatoluide* (m. p. 184°), which is soluble in alcohol and ether.

The *sulphate*, $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_4.\text{H}_2\text{SO}_4$, *hydrochloride*, *nitrate*, and *oxalate* are crystalline salts, soluble in water.

Anhydro-compounds from Xylidine.—The preparation of α -benzoyl-xylidine, α -mononitrobenzoxylidine, and α -anhydrodiamidobenzoxylene from α -xylidine and of the corresponding β -compounds from β -xylidine, have been already described by F. Boyes (*Ber.*, 10, 143, this Journal, Abstr., 1878, 143). The α -anhydro-base—



crystallises in colourless needles (m. p. 195°), soluble in alcohol.

The *hydrochloride*, $\text{C}_{15}\text{H}_{14}\text{N}_2.\text{HCl}$, *oxalate*, *nitrate*, and *sulphate* form needle-shaped crystals. All these salts, with the exception of the sulphate, dissolve readily in alcohol and in water.

The corresponding β -compound forms colourless needles (m. p. 215°), soluble in alcohol. The sulphate and hydrochloride also form needle-shaped crystals which are easily soluble in water.

The properties and mode of preparation of *paranitrobenzamidonaphthalene* (m. p. 224°), *paramidobenzamidonaphthalene* (m. p. 186°), β -nitroorthobenzamidonaphthalene (m. p. 175°), *anhydrobenzoyldiamidonaphthalene* (m. p. 210°), *dinitrobenzamidonaphthalene* (m. p. 252°), *dinitramidonaphthalene* (m. p. 233°), and *diamidobenzamidonaphthalene* have already been described by Ebell (*Ber.*, 7, 1317; 8, 562).

From these facts the author concludes that it is only the *ortho*-diamido-compounds which have the power of losing a molecule of water and forming anhydro-bases, when subjected to the powerful action of nascent hydrogen.

W. C. W.

Dinitro- and Trinitro-resorcinol. By R. BENEDIKT and A. v. HÜBL (*Monatsh. Chem.*, 2, 323—330).—Fitz, who discovered dinitroso-resorcinol (*Ber.*, 1875, 631), did not succeed in converting it into dinitro-resorcinol, but found that nitric acid, even when very dilute, converts it at once into trinitroresorcinol, and that when heated with potassium permanganate or ferricyanide, even in the cold, it is completely oxidised and burnt. Weselsky and Benedikt however have shown that nitroso-compounds can be oxidised to nitro-compounds by exposing them suspended in ether to the action of nitrous acid vapours (p. 726 of this volume), the vapour being passed through the liquid for several hours, and the reaction being completed when the nitroso-compound is entirely dissolved. The product must be repeatedly shaken with water to remove oxides and acids of nitrogen dissolved in the ether, and the ether may then be distilled off, but not completely, as in that case, a small quantity of nitric acid which

remains behind in spite of the agitation with water, would induce a further nitration to trinitro-resorcinol. The product is then poured out into a small basin, the ether left to evaporate at ordinary temperatures, and the residue, after pulverisation, thoroughly washed with cold water. It may then be crystallised from dilute alcohol without fear of further nitration.

Dinitroresorcinol crystallises in pale yellow laminæ, melts at 142° , is partially sublimable, and detonates when strongly heated. When heated with very dilute nitric acid (*e.g.*, 1 : 10) it is completely converted into trinitro-resorcinol. Its *potassium salt* crystallises in orange-yellow easily soluble prisms. The *ammonium salt* forms reddish-yellow geodes having a satiny lustre. The *normal barium salt*, $C_6H_2(NO_2)_2O_2Ba$, prepared by boiling dinitroresorcinol with barium carbonate, crystallises on cooling in geodes of small yellow needles nearly insoluble in cold water.

Nitro-amidoresorcinol, $C_6H_2(NO_2)(NH_2)(OH)_2$, is obtained as an ammonium salt by passing hydrogen sulphide into a solution of dinitroresorcinol (50 g.) in 356 c.c. absolute alcohol mixed with 150 c.c. aqueous ammonia and heated to about 70° . The yellow pulpy ammonium salt which forms at first dissolves slowly to a clear dark-red liquid, whereupon the stream of gas must be interrupted, and the liquid left at rest for twelve hours. The ammonium salt then separates in dark-coloured needles traversing the whole liquid; and on draining off the mother-liquor, dissolving the crystals in water, filtering from sulphur, and cautiously adding dilute sulphuric acid as long as a precipitate is formed, but no longer, free nitroamidoresorcinol is obtained as a brown crystalline precipitate, which may be purified by recrystallisation from weak spirit. It then forms black-brown crystals sparingly soluble in water, easily in alcohol and ether, melting at about 170° . It dissolves easily in acids and in alkalis. The alkali salts reduce ammoniacal silver solution, even at ordinary temperatures, and form with lead salts a red-brown flocculent precipitate; with barium salts, after a while, a black crystalline precipitate. The ammonium salt, as already observed, separates on reduction of dinitroresorcinol in alcoholic solution, in slender needles mixed with sulphur, which may be easily removed by washing with carbon bisulphide, the purified ammonium salt then forming dark violet crystals containing a variable quantity of ammonia. The salt when recently prepared has the normal composition $C_6H_2(NO_2)(NH_2)(ONH_4)_2$, but gives off part of its ammonia on mere exposure to the air, and after several days' drying at 100° is completely reconverted into free nitroamidoresorcinol. In aqueous solution, the ammoniacal salt is very unstable, and is completely decomposed on heating, with formation of resinous products.

Nitramidoresorcinol sulphate, $[C_6H_2(OH)_2(NO_2)(NH_2)]_2SO_4H_2$, forms brownish slender needle-shaped crystals easily soluble in water and decomposing at 100° .

Dinitro-amidoresorcinol, $C_6H(OH)_2(NO_2)_2.NH_2$, or *Styphnamic acid*, the analogue of picramic acid, is obtained on prolonged heating of styphnic acid (trinitroresorcinol) dissolved in alcohol with ammonium sulphide, and purified by acidulating the resulting solution with acetic

acid, repeatedly agitating it with ether, then distilling off the ether, and recrystallising the crude product from absolute alcohol.

Styphnic acid forms copper-red shining laminæ, nearly insoluble in water, only slightly soluble in alcohol, but dissolving readily in alkalis, and precipitated therefrom by dilute acids only at the boiling heat. It dissolves easily in strong sulphuric acid, forming a colourless liquid, from which it is precipitated by water in red laminæ.

Dinitrodiazo-resorcinol, $C_6H_2N_4O_6 = HO.N:N.C_6H \left\{ \begin{smallmatrix} (NO_2)_2 \\ O \end{smallmatrix} \right.$.—The potassium salt of this compound is obtained by dissolving 5 g. mono- or di-nitramido-resorcinol in 155 c.c. sulphuric acid diluted with 5 volumes of water, adding an excess of potassium nitrite in aqueous solution, and boiling till the liquid turns greenish-yellow. On cooling, the entire liquid solidifies to a light-yellow crystalline mass of the potassium salt, which may be purified by recrystallisation, and separates from very strong aqueous solutions, or from dilute sulphuric acid, or on mixing its solution with alcohol, in long slender anhydrous crystals, having a fine yellow colour without surface-shimmer. By slow crystallisation from dilute aqueous solution, it is obtained in compact brown prisms with blue surface-shimmer, having the composition $C_6HN_4O_6K + H_2O$. This salt is highly explosive, decomposing with violent detonation when heated, struck, or pressed. It is very soluble in hot, very sparingly in cold water. It does not appear possible to introduce more than 1 atom of potassium into dinitrodiazo-resorcinol, the monopotassic salt crystallising out unaltered from its solution mixed with the calculated quantity of potassium carbonate.

Free dinitrodiazo-resorcinol is obtained by dissolving the potassium salt in dilute sulphuric acid, the colourless liquid, on exposure to the air, depositing it in yellow triclinic crystals which detonate when heated.

Mononitrodiazo-resorcinol is formed on mixing a solution of nitro-amido-resorcinol in dilute sulphuric acid with the calculated quantity of potassium nitrite in cold aqueous solution, and separates from the liquid as a brown crystalline precipitate, which may be recrystallised from alcohol.

Action of Potassium Hydroxide on Dinitrodiazo-resorcinol.—When a solution of the above-described potassium salt is boiled with potassium hydroxide, its colour quickly changes from light yellow to red; nitrogen is abundantly evolved; and on acidulating the liquid, the greater part of the product separates as a flocculent precipitate, which, on recrystallisation from absolute alcohol, yields two bodies, one (A) the chief product of the reaction, separating in granular shining crystals; whilst the other (B) is deposited from the mother-liquors in light-brown laminæ. This latter body is the sole product obtained when the reaction takes place in alcoholic instead of aqueous solution, and may then be separated by diluting the alcoholic liquid with water, acidulating with sulphuric acid, and purified by crystallisation from strong alcohol.

The body A is slightly coloured, nearly insoluble in water, slightly soluble in alcohol, easily in ether and strong acetic acid. It melts at 268° . Its analysis agrees nearly with the formula of *tetranitrodiazo-resorcinol*, $C_{12}H_6N_4O_{12} = (OH)_2(NO_2)_2HC_6.C_6H(NO_2)_2(OH)_2$, which is a

diphenyl-derivative, a view which is supported by its high melting point, and by the circumstance that it is not susceptible of further nitration, but crystallises unaltered from solution in boiling nitric acid. It dissolves in potassium carbonate, the solution on cooling depositing the acid potassium salt, $C_{12}H_4K_2N_4O_{12}$, in shining red needles; and by mixing the solution of this salt with potassium hydroxide, the normal salt is obtained in needle-shaped crystals, having a dark green colour and metallic lustre.

The body B, obtained by the action of alcoholic potash on dinitro-diazo-resorcinol, forms large light brown shining laminæ, melts at 210° , and is sublimable: it is very slightly soluble in boiling water, more readily in alcohol. According to its analysis, it might be regarded as a new dinitro-resorcinol; but this view is inconsistent with the fact that it is completely unattacked by strong boiling nitric acid.

H. W.

Quinone Derivatives. By E. SARAUW (*Annalen*, 209, 93—131).—Quinone when treated with hydrobromic acid yields a mixture of mono- and di-bromoquinol, with the intermediate production of quinhydrone. This reaction may be explained thus: at first quinhydrone is formed with liberation of bromine; the former is converted by excess of hydrobromic acid into monobromoquinol, whilst the latter reacts with the unattacked quinone, forming monobromoquinone and hydrobromic acid; and finally the monobromoquinone combines with the hydrobromic acid to form dibromoquinol. Wöhler in the study of the analogous action of concentrated hydrochloric acid (*Annalen*, 51, 155) noticed the formation of a dark coloration in the earlier part of the reaction, which he concluded to be due to an intermediate product of the formula $C_6H_4(OH)(OCl)$. The author, however, shows that the actions of hydrochloric and hydrobromic acids are precisely similar, and that the dark coloration is due to quinhydrone.

Monobromoquinol, $C_6H_3Br(OH)_2$.—Owing to the difficulty of separating the mono- and di-bromoquinol in the above reaction, the monobromoquinol is best prepared by the direct reaction of equal molecules of bromine and quinol in chloroform solution (comp. Abstr., 1880, 385). Monobromoquinol crystallises in delicate leaflets (m. p. 110°), soluble in water, benzene, &c.; sparingly soluble in chloroform and petroleum.

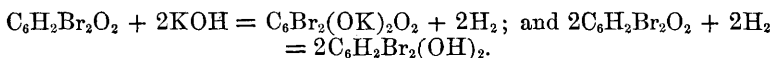
Monobromoquinone, $C_6H_3BrO_2$, is obtained by the oxidation of monobromoquinol with ferric chloride. It crystallises in tufts of needles (m. p. 55 — 56°), easily soluble in chloroform, ether, alcohol, &c.; sparingly soluble in petroleum and in hot water. Monobromoquinone dissolves in ammonia and in sodium hydroxide or carbonate, to form a dark black solution; it is probable that the bromine-atom is displaced by the hydroxyl-group, and a body of formula, $C_6H_3(OH)O_2$, is produced.

Dibromoquinol, $C_6H_2Br_2(OH)_2$, is prepared either by the action of hydrobromic acid on monobromoquinone, or of 2 mols. bromine on 1 mol. quinol, or of 1 mol. bromine on 1 mol. quinone. It crystallises in tablets (m. p. 186 — 187°), soluble in alcohol and ether, sparingly soluble in benzene, carbon bisulphide, &c.

An isomeric dibromoquinol of probable formula $C_6H_3Br(OH)(OBr)$ is obtained in the preparation of ordinary dibromoquinol from quinone.

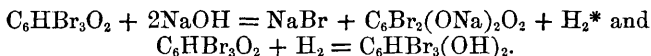
This body crystallises in golden rhomboidal tables (m. p. 86—87°). After a few days, it is converted into the above dibromoquinol (m. p. 186°). Whatever may be the constitution of this isomeride, it is at least probable that one bromine-atom is not in the benzene nucleus, for it is decomposed readily by water, with formation of hydrobromic acid and quinone. It is soluble in ether, carbon bisulphide, chloroform, &c.; sparingly soluble in petroleum.

Dibromoquinone, $C_6H_2Br_2O_2$, is prepared by the oxidation of dibromoquinol with ferric chloride; it crystallises in delicate needles (m. p. 188°), soluble in ether, benzene, and alcohol, insoluble in water. Dibromoquinone dissolves in sodium hydroxide, forming a deep brown solution, from which glistening black prisms of sodium bromanilate separate. On saturating the alkaline filtrate from this salt and extracting the precipitate with ether, dibromoquinol is formed. Hence the reaction of sodium hydroxide on dibromoquinone may be expressed thus—



Tribromoquinol, $C_6HBr_3(OH)_2$, is obtained together with tetrabromoquinol by heating dibromoquinone with concentrated hydrobromic acid; but it is best prepared by the action of 3 mols. bromine on 1 of quinol, or by the action of 2 mols. bromine on 1 of quinone. Tribromoquinol crystallises in grouped needles (m. p. 135°), easily soluble in alcohol, chloroform, benzene, &c.

Tribromoquinone, $C_6HBr_3O_2$, is prepared by the oxidation of tribromoquinol with ferric chloride. It forms golden-yellow leaflets (m. p. 147°), soluble in alcohol, ether, benzene, &c. The action of sodium or potassium hydroxide on tribromoquinone and trichloroquinone is precisely analogous, sodium bromanilate and tribromoquinol being formed thus—



Tetrabromoquinol, $C_6Br_4(OH)_2$, is prepared by the action of concentrated hydrobromic acid on tribromoquinone or bromanil, or of 4 mols. bromine on quinol.

Bromanil, $C_6Br_4O_2$, is obtained by the action of excess of bromine on quinone or quinol; solutions of the alkalis replace 2 bromine-atoms in it by 2 hydroxyl-groups.

Action of acetic anhydride on quinone (see Abstr., 1879, 718).

V. H. V.

Ethylenic Ethers of Phenol and Nitrophenol. By A. WEDDIGE (*J. pr. Chem.* [2], **24**, 241—256).—In a former notice, it was shown that the action of ethylene bromide on the alkali salts of ortho- and para-nitrophenol produced either bromethylene nitrophenyl ether or ethylene dinitrophenyl ether, according as to whether 1 or 2 mols. of the salt entered into the reaction. Researches which have lately been made with the alkali salts of other hydroxyl-compounds of the aro-

* This equation is wrong (also in the original paper); it should perhaps be:—

$$CHBr_3O_2 + 3NaOH = NaBr + C_6Br_2(ONa)_2O_2 + H_2O + H_2. \quad [Ed.]$$

matic series have shown that analogous reactions occur in such cases, and compounds corresponding with those mentioned above can be prepared. The ortho-series of these compounds has been therefore more carefully studied, to determine the composition of the remarkable condensation-products which can be obtained from this series.

Bromethylene phenyl ether was prepared from ethylene bromide and sodium phenol purified by distillation and crystallisation, when it was found to melt at 39° , to boil at $240\text{--}250^{\circ}$ (not without decomposition) and to be readily soluble in ether and alcohol, but only sparingly in water.

Imidodiethylenephenyl ether hydrobromide, $\text{HN}(\text{C}_2\text{H}_4\text{O.C}_6\text{H}_5)_2\text{HBr}$, is produced by heating bromethylene-phenyl ether with alcoholic ammonia. Water added to the mixture after removal of alcohol removes ammonium bromide, and the residue heated with sodium hydroxide yields an oily base, of which the acetate is the only salt easily soluble in water. The pure hydrobromide can be recrystallised from hot water in silky colourless needles, which darken when heated to 216° . Aqueous solutions of the alkalis decompose the salt, but not as alcoholic solutions. The hydrochloride (m. p. 213°) is precipitated on adding hydrochloric acid to a solution of the acetate: in fact this method is general for the formation of these salts. The nitrate (m. p. 197°) is colourless; the chromate when precipitated resembles lead chromate in colour, but when crystallised from hot water it is dark yellow, becoming brown in the air. The sulphate, which next to the acetate is the most soluble in water, forms plates of a pearly lustre. No primary base produced by the action of ammonia on bromethylene-phenyl ether appears to resist.

Ethylene-phenylorthonitrophenyl ether, $\text{OPhC}_2\text{H}_4\text{O.C}_6\text{H}_4\text{NO}_2$, is produced by heating a mixture of equal molecules of bromethylene phenyl ether and potassium orthonitrophenol at $120\text{--}130^{\circ}$ in sealed tubes; it crystallises from hot alcohol, in which it is sparingly soluble, in small colourless prisms (m. p. 86°).

Bromethylene orthonitrophenyl ether, $\text{C}_2\text{H}_4\text{Br.O.C}_6\text{H}_4\text{NO}_2$, is prepared by dissolving sodium orthonitrophenol and ethylene bromide in alcohol, and then heating the mixture on a water-bath until all colour disappears. Another substance seems to be simultaneously produced (m. p. 117°), yielding under the influence of the action of hydrochloric acid on tin a reduction-product (m. p. $98\text{--}100^{\circ}$); at present this compound has not been further investigated.

The original bromo-derivative is of a pale yellow colour, crystallising in large thick prisms (m. p. $43\cdot5^{\circ}$), insoluble in water.

Amidoethylene-orthonitrophenyl ether, $\text{NH}_2\text{.C}_2\text{H}_4\text{O.C}_6\text{H}_4\text{NO}_2$, is formed by the action of excess of alcoholic ammonia on the bromo-ether at $100\text{--}120^{\circ}$; freed from alcohol and ammonium bromide, the mass appears of a dark red colour, and when treated with hydrochloric acid the amido-ether is dissolved, whereas the chlorides of the imido-ether which are simultaneously produced remain behind. The amido-ether crystallises from hot water in small plates (m. p. $72\text{--}73^{\circ}$) of a cinnabar colour, sparingly soluble in water: the alcoholic or ethereal solutions are not red but yellow, the red colour reappears, however, on evaporation of the ether. Nascent hydrogen reduces the nitro-

grouping, forming a base $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, whose solution exposed to the air becomes of a deep red colour, and is oxidised by ferric chloride to a green mass, which as yet has not been further investigated.

Imidodiethylene-orthonitrophenyl ether, $[\text{NH}(\text{NO}_2)\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_4]_2$, is prepared as stated above, and crystallises from water or alcohol in pale yellow needles (m. p. 191—192°). The free base dissolved in alcohol appears yellow.

Benzoylamidoethylene-orthonitrophenyl ether, $\text{NH}\cdot\text{Bz}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is formed with evolution of hydrochloric acid. When the amido-ether and benzoic chloride are mixed, two substances are produced, one of which is orange and the other pale yellow; the orange-coloured substance is the monobenzoyl-derivative, the most insoluble in alcohol, whereby it can be separated from the pale yellow dibenzoyl-compound. The monobenzoyl ether (m. p. 94—95°) is indifferent to acids or alkalis. It is reduced by tin and hydrochloric acid with formation of *anhydrobenzoylamidoethylenorthamidophenyl ether*,



(m. p. 149—151), which may be crystallised from benzene. It unites readily with acids. The sulphate when oxidised is converted into a cherry-red liquid. It has yet to be determined whether the composition of this body is most correctly represented by the formula $\text{C}_2\text{H}_4\left\langle\begin{array}{c} \text{—NH—} \\ \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N=} \end{array}\right\rangle\text{C}_7\text{H}_5$, or by $\text{C}_2\text{H}_4\left\langle\begin{array}{c} \text{—N=} \\ \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH} \end{array}\right\rangle\text{C}_7\text{H}_5$.

Dibenzoylamido-ether, $\text{N}\cdot\text{Bz}_2\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, can also be prepared by treating the amido-ether with excess of benzoic chloride. It forms yellow needles (m. p. 121—122°), insoluble in water. No crystallised reduction-product has as yet been prepared.

Hydroxyethylene-orthamidophenyl Ether, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.—As the action of reducing agents on the hydroxyethylene nitro-ether did not give satisfactory results, the benzoate was chosen as a starting point. Potassium benzoate and the bromo-ether were heated with alcohol at 130—140°; after separation of the alcohol and recrystallisation, long silky needles (m. p. 76°) were produced, but no direct anhydro-compound could be obtained by reduction.

Tin and hydrochloric acid remove the benzoic group, forming the hydroxyethylene ether, whilst zinc-dust and ammonia only reduce the nitro-grouping, $\text{Bz}\cdot\text{O}_2\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. The hydroxyethylene ether appears as pearly colourless plates, which when heated become of a brown violet, and melt at 89—90°. It is but slightly soluble in water, and crystallises best from benzene. Being a strong base, it forms easily soluble salts with acids, and is converted by oxidation into a red-brown dye. Distillation with benzoic chloride produces a base melting at 102°. Probably this substance is the same as that obtained by Ladenburg from orthamidophenol and acid chlorides. That compound—formed under the influence of zinc and ammonia—melts at 98—100°, is basic, and forms salts; dry distillation producing from it benzoic acid, and a new base as yet not investigated.

Bromethylene-paranitrophenyl ether is analogous to the ortho-compound, and is prepared by using sodium paranitrophenol in place

of the ortho. It crystallises from pure alcohol in three-sided tables (m. p. 63—64°), and is insoluble in water.

Amidoethylene paranitrophenyl ether is formed as a secondary base by heating the brom-ether with alcoholic ammonia, as in the case of the ortho body. Crystallised from hot water it is yellow, resembling lead iodide (m. p. 108°). Reduction produces a base, which when oxidised does not yield a dye, but a quinone.

Bromethylene-metanitrophenyl ether, prepared by a process analogous to that employed for the formation of the ortho- and para-compounds, melts at 39°, is white, and insoluble in water. Alcoholic ammonia causes the production of a colourless base. If the three bromethylene nitrophenyl ethers dissolved in alcohol are heated with the alkali salts of the three nitrophenols, the six ethylene dinitrophenyl ethers are formed, and these will be described later. Similar treatment of the bromo-compounds with potassium salts of salicylic ether yield an ether,

$C_2H_4 \begin{smallmatrix} < OC_6H_4.COOEt \\ < OC_6H_4.NO_2 \end{smallmatrix}$, which is converted into the free acid by the action of hydrochloric acid, C_2H_5 being eliminated. This acid has been obtained pure, and has been analysed; that produced from the bromethylene orthonitro-ether melts at 143°; that from the para-compound at 130°.

E. W. P.

Ethers of Quinol and Orcinol. By P. WESELSKY and R. BENEDIKT (*Monatsh. Chem.*, 2, 369—371).—This paper gives an account of the results obtained by the action of nitric acid containing nitrous acid (Weselsky's reagent, p. 726) on the methylic and ethylic ethers of quinol and orcinol. Monomethyl- and monethyl-quinol thus treated each yield three bodies, one of which separates in yellow needles from the ethereal solution when mixed with green nitric acid; but the quantity obtained was not sufficient for analysis.

The product obtained from monethyl-quinol fused, after recrystallisation from chloroform, at 213°, decomposing at the same time. It is insoluble in water, ether, alcohol, and cold aqueous potash. When heated with the latter, it yields a red solution, from which acids throw down an amorphous flocculent precipitate, perhaps related to nitranilic acid.

The ethereal mother-liquors still contain two products, viz., a mononitroquinol ether, volatile with aqueous vapour, and a non-volatile dinitroquinol ether, which may be separated by distillation in a current of steam, as described in the authors' former paper (p. 727 of this volume) and purified by recrystallisation from dilute alcohol. *Methylic mononitroquinol*, $C_6H_3(NO_2)(OMe).OH$, forms orange-yellow needles something like orthonitrophenol, and melting at 83°. *Methylic dinitroquinol*, $C_6H_2(NO_2)_2(OMe).OH$, forms turbid, greenish flat needles, melting at 102°. It dissolves in warm potassium hydroxide, the solution on cooling depositing the potassium salt in long needles, having a bright green lustre. *Ethylic nitroquinol*, $C_6H_3(NO_2)(OEt).OH$, crystallises in needles having a deep yellow colour, smelling like the volatile nitrophenols, and melting at 83°.

Ethylamidoquinol hydrochloride, $C_6H_3(NH_2)(OEt)OH.HCl$, obtained by reduction of the nitro-compound, forms large compact

crystals. Its solutions are moderately permanent in the air. *Ethyllic dinitroquinol*, $C_6H_2(NO_2)_2(OEt).OH$, forms brownish needles melting at 71° .

Orcinol-ethers.—Mono- and di-ethylorcinol yield similar products, viz., volatile and non-volatile mononitroethylic ethers, together with a small quantity of a dye-stuff soluble in ether, and crystallising from alcohol in shining microscopic needles, insoluble in potash, but soluble with splendid blue-violet colour in strong sulphuric acid. *Volatile ethylic nitro-orcinol*, $C_6H_2Me(NO)(OEt).OH$, crystallises in slender yellow needles melting at 54° ; the *non-volatile ether* in yellow needles melting at 103° . H. W.

Direct Introduction of Carboxyl-groups into Phenols and Aromatic Acids. PART IV.* *Reaction of Quinol with Potassium Hydrogen Carbonate.* By C. SENHOFER and F. SARLAY (*Monatsh. Chem.*, 2, 448).—When quinol is heated in a sealed tube with four times its weight of hydrogen-potassium carbonate and an equal quantity of water—with addition of potassium sulphite or other reducing agent to prevent the formation of dark-coloured oxidation-products on exposure of the product to the air—and this product is exhausted with ether, the residue being strongly acidulated with sulphuric acid, and again treated with ether, the first extract yields, on removal of the ether by distillation, a considerable quantity of unaltered quinol, whilst the second on evaporation leaves a mass which when purified by crystallisation from water, with addition of animal charcoal, and subsequent treatment with toluene in an extraction apparatus, yields colourless crystals of a dihydroxybenzoic acid, exhibiting the reactions of a hydroxysalicylic acid, while its formation from quinol shows that it must have the constitution $OH : COOH : OH = [1 : 2 : 4]$. It melts at 197° ; its aqueous solution is not precipitated by lead acetate, but gives with ferric chloride a deep blue coloration, which sometimes lasts for a considerable time, and changes on addition of a very dilute solution of acid potassium or sodium carbonate to violet, and on further addition to red. It reduces the oxides of silver and copper in alkaline solution. It dissolves readily in alcohol, ether, and warm water, somewhat less readily in cold water, also in dilute sulphuric and hydrochloric acids. When distilled with pumice, it yields quinol.

The *copper salt* of this acid crystallises in concentric groups of long needles, having the composition $C_{14}H_{10}O_8Cu + 4\frac{1}{2}H_2O$. The *lead salt*, $C_{14}H_{10}O_8Pb + 2H_2O$, crystallises from aqueous solution in felted groups of slender needles, sparingly soluble in cold water, and giving off their crystal-water at 150° . The *sodium salt*, $C_7H_5O_4Na + 5\frac{1}{2}H_2O$, separates from concentrated solution in large flat prisms, which give off 5 mol. H_2O at 100° . The *potassium salt* crystallises in large well-defined prisms, which have the composition $C_7H_5O_4K + H_2O$, and give off their water at 160° . The *calcium salt* separates from concentrated solution in slender shining needles, having, when air-dried, the composition $C_{14}H_{10}O_8Ca + 7H_2O$, and giving off their water at 160° .

* For abstracts of the first three papers of this series, by Senhofer and Brunner, see p. 265 of this volume.

Hydroxysalicylsulphonic or *Sulphohydroxysalicylic acid*, $C_7H_5SO_7 = C_6H_2(OH)_2(COOH).SO_3H$, is prepared by heating a solution of 1 pt. hydroxysalicylic acid in 5 pts. strong sulphuric acid with 1 pt. phosphoric anhydride for some time at 130° , diluting the liquid, after cooling, with water, treating it with ether to remove a small quantity of unaltered hydroxysalicylic acid, then boiling it with barium carbonate and filtering quickly. The filtrate on cooling deposits a micro-crystalline barium salt, which is nearly insoluble in water, but dissolves in warm dilute hydrochloric acid, the solution on cooling depositing an acid barium salt in hard slender needles, which may be purified by recrystallisation from hot water. Their solution has a strongly acid reaction, and gives a splendid blue colour with ferric chloride. The crystals in the air-dried state have the composition $(C_7H_5SO_7)_2Ba + 8\frac{1}{2}H_2O$, and give off $7\frac{1}{2}$ mol. H_2O at 130° .

The *normal barium salt*, prepared from the acid salt by neutralisation with barium carbonate, crystallises in microscopic four-sided laminae, having in the air-dried state the composition $C_7H_4SO_7Ba + 2H_2O$, and giving off $1\frac{1}{2}$ mol. H_2O at 130° . The *lead salt*, prepared by decomposing the barium salt with the exact quantity of sulphuric acid required, and treating the filtrate with lead carbonate, is a crystalline powder having, when air-dried, the composition $C_7H_4SO_7Pb + H_2O$, and giving off half its water at 130° . The *potassium salt* forms small four-sided prisms, not very soluble in cold water. When air-dried they contain $C_7H_4SO_7K_2 + H_2O$, and give off their water at 150° .

The free acid, obtained by the decomposition of the lead salt, forms colourless or yellowish needles, but as hitherto prepared, always contains a small quantity of sulphuric acid, doubtless arising from decomposition.

PART V. *Action of Acid Potassium Carbonate on Toluquinol*. By C. BRUNNER (*Monatsh. Chem.*, **2**, 458—467).—40 grams toluquinol, 130 acid potassium carbonate, 110 c.c. water, and 40 c.c. concentrated solution of potassium sulphite, were enclosed in a digester and heated for 36 hours in a bath of turpentine oil. The product acidulated with dilute sulphuric acid yielded a crystalline deposit of a new acid, and on agitating the whole with ether, which dissolved both this and the unaltered toluquinol, and treating the ethereal liquid with a solution of ammonium carbonate, the acid passed into the aqueous solution as ammonium salt, from which it was separated by acidulation and renewed agitation with ether. On distilling off the ether, the acid remained in brown crystalline crusts, amounting to 40—45 per cent. of the toluquinol employed. For purification, it was dissolved in hot water, the solution on cooling yielding two kinds of crystals, one kind indistinctly developed, while the other consisted of small well-defined white prisms. These, however, consisted of the same organic acid, hydrated and anhydrous. To free them from a yellow-brown coloration which obstinately adhered to them, they were dissolved in hot water, the solution neutralised with lead carbonate, and the dissolved lead thrown down by hydrogen sulphide. The liquid filtered from the lead sulphide deposited on cooling slightly yellow crystalline masses, the solution of which in dilute alcohol yielded the new acid in well-defined

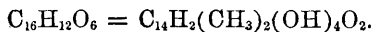
microscopic twin-crystals of oblique rhombic habit. The analysis of these crystals gave 56·73 to 37·33 per cent. carbon, and 4·39 to 5·01 hydrogen, leading to the formula $C_8H_5O_4$, which requires 57·14 C and 4·76 H. This composition was corroborated by the analysis of several salts, viz., the potassium salt, $C_8H_5O_4K$, which crystallises anhydrous, and the barium, calcium, and lead salts, $(C_8H_5O_4)M''$, which crystallise with $2H_2O$. The *ethylic ether*, $C_8H_5O_4.C_2H_5$, prepared in the usual way, crystallises in white felted anhydrous needles, nearly insoluble in cold, slightly soluble in warm water, freely in alcohol and ether. With ferric chloride the aqueous solution of the acid gives an azure-blue colour, changing on standing, or on further addition of ferric chloride, to a fine green. It reduces an alkaline cupric solution immediately on heating, slowly in the cold; silver solution immediately even in the cold.

The acid above described is isomeric with homoprotocatechuic, orsellinic, and para-orsellinic acids, but is distinguished from the two former by its sparing solubility, high melting point, and reaction with ferric salts, and from the last also by its melting point and by its reaction with silver salts.

From the analogy of toluquinol to quinol, this acid might be expected to exhibit properties analogous to those of hydroxysalicylic acid; and having regard to these relations, the authors designate it as Homohydroxysalicylic acid.

When gradually heated to $210-220^\circ$, this acid is resolved, for the most part, into carbonic anhydride and toluquinol, which is soluble in ether; a small quantity of substance insoluble in ether, probably a condensation product, being formed at the same time.

When homohydroxysalicylic acid is gently heated with four times its weight of strong sulphuric acid, it dissolves with fine green colour, and is precipitated from the solution by water without alteration; but if the temperature be raised to $120-300^\circ$ for four or five hours, and the mass after cooling be thrown into water, red flocks are abundantly precipitated; these after decantation and washing, leave a dark red powder only sparingly soluble in the greater number of solvents. On repeatedly digesting it with acetone, and filtering, the first filtrates exhibit a deep red colour, while the latter ones are but slightly coloured, and ultimately there remains a body which when dissolved in warm potassium hydroxide and reprecipitated by hydrochloric acid, has the composition of *dimethyl-tetrahydroxyanthraquinone*,



This compound is but very slightly soluble in water, alcohol, and ether, somewhat more soluble in acetone and glacial acetic acid, especially when heated; wool and silk boiled with it in water are dyed pale violet. It dissolves in potash with green colour at ordinary, blue at higher temperatures, and is reprecipitated therefrom by acids in its original state. Heated in a stream of carbonic anhydride, it sublimes in crimson needles, appearing under the microscope as flattened prisms, and melting above 300° . When heated with zinc-dust it yields a solid sublimate, probably dimethylantracene, but the quantity obtained was too small for analysis. It dissolves easily in hot glacial acetic

acid, and crystallises therefrom on cooling. From a hot concentrated alcoholic solution, it separates in prismatic crystals, having a faint yellow colour. After repeated crystallisation from glacial acetic acid and carbon bisulphide, it melts at 242° .

The extracts obtained, as above stated, on treating the red colouring matter with acetone, leave on evaporation of the solvent, a red substance, consisting mainly of the body sparingly soluble in acetone; but the presence of another body is shown by the fact that, on heating the substance in a stream of carbonic anhydride, the flat red prisms above mentioned are accompanied by well-defined yellowish needles, which dissolve in potash with yellowish-red colour, and are not precipitated therefrom by hydrochloric acid. The author is engaged with the further examination of these bodies.

H. W.

Addition-products of Atropic Acid. By G. MERLING (*Annalen*, 209, 1—21).— α -Chlorhydratropic acid, $\text{CH}_2\text{Cl}.\text{CHPh}.\text{COOH}$, is obtained by the action of fuming hydrochloric acid at 100° , or in the cold on atropic acid. It crystallises in colourless right-angled tables (m. p. 86 — 88°), which decompose at about 170° . If this acid in aqueous solution is heated for some time with potassium carbonate, tropic acid is formed, together with some small quantity of styrolene and atropic acid; 73 per cent. of the chloro-acid being decomposed thus: $\text{C}_9\text{H}_9\text{ClO}_2 + \text{H}_2\text{O} = \text{C}_9\text{H}_{10}\text{O}_3 + \text{HCl}$.

β -Chlorhydratropic acid, $\text{CH}_3.\text{CClPh}.\text{COOH}$, is obtained by dissolving atrolactic acid in fuming hydrochloric acid. It differs from the isomeric α -acid by melting at 73 — 74° , decomposing at 110° , and giving no styrolene when heated with alkaline carbonates.

α -Bromhydratropic acid, $\text{CH}_2\text{Br}.\text{CHPh}.\text{COOH}$, is formed by heating atropic acid with fuming hydrobromic acid at 100° in sealed tubes. It crystallises in small prisms (m. p. 93 — 94°), soluble in alcohol, ether, and benzene, insoluble in water. It resembles the corresponding α -chloro acid in giving with the alkaline carbonates styrolene, tropic and atropic acids. It decomposes when heated to 150° .

α -Amidohydratropic acid, $\text{NH}_2.\text{CH}_2.\text{CHPh}.\text{COOH}$, is obtained by dissolving α -bromhydratropic acid in ammonia. It crystallises in glistening leaflets, or slender needles (m. p. 169 — 170°).

β -Bromhydratropic acid, $\text{CH}_3.\text{CBrPh}.\text{COOH}$.—By the action of cold concentrated hydrobromic acid on atropic acid, Fittig (*Abstr.*, 1879, 379) obtained a bromhydratropic acid which melted at the same temperature (93 — 94°) as the author's α -bromhydratropic acid, and gave with ammonia an amidohydratropic acid, identical in melting point (169.5°) with the α -amidohydratropic acid above. Hence it would appear that the acids obtained by Fittig and by the author were identical. The author finds, however, that by the action of hydrobromic acid on atrolactic acid, or by the combination of atropic acid with hydrobromic acid at 0° , an acid is formed which, although it has the same melting point as the α -acid, yet differs from it by decomposing at 100° , and in giving no styrolene when heated with alkaline carbonates. The action of ammonia on this β -bromhydratropic acid was further examined, and it was proved that β -amidohydratropic acid was not formed. The author explains Fittig's results on the supposition that he used for

the preparation of his amidohydratropic acid the mixture of α - and β -bromhydratropic acids, which result from the combination of atropic and hydrobromic acid at ordinary temperatures. V. H. V.

Action of Benzoic Chloride on Glycocine-silver. By T. CURTIUS (*J. pr. Chem.* [2], **24**, 239).—By the action of benzoic chloride on glycocine-silver, three nitrogenous acids are formed. They are easily soluble in hot water, but the first, $C_9H_9NO_3$ (m. p. 186.5°), is hippuric acid, and is identical with the acid found in the animal organism. The second acid, $C_{11}H_{12}N_2O_3$ (m. p. 206.5°), being insoluble in boiling chloroform, is therefore easily separated from the hippuric acid. In the same manner as hippuric acid assimilates 1 mol. water, and breaks up into benzoic acid and glycocine, so this acid when boiled with acids assimilates 2 mols. H_2O , and breaks up into 1 mol. benzoic acid and 2 mols. glycocine; it must therefore be considered as hippuryl glycocine, $CH_2NH(CH_2NHBz.CO)COOH + 2H_2O = 2CH_2NH_2.COOH + BzOH$. The third acid, $C_{10}H_{12}N_3O_4$, darkens at 240° , is insoluble in alcohol and in chloroform. Boiling with acids likewise converts it into benzoic acid and glycocine, but at the same time a third substance is formed, which has not yet been isolated and examined. E. W. P.

Nitrosulphobenzoic Acids and some of their Derivatives. By E. HART (*Am. Chem. J.*, **1**, 340—356).—Two nitrosulphobenzoic and three amidosulphobenzoic acids have been known for some time, but the relative positions of their substituted radicles have not been determined. Mulder in 1840 (*Annalen*, **34**, 302) obtained a nitrosulphobenzoic acid by heating metanitrobenzoic acid with fuming sulphuric acid. Limpricht and Uslar in 1858 (*ibid.*, **106**, 27) prepared another nitro-acid by direct nitration of metasulphobenzoic acid, and converted it by reduction into the corresponding amido-acid. Griess in 1872 (*J. pr. Chem.* [2], **5**, 244), by treating metamido-benzoic acid with sulphuric acid, obtained two amidosulphobenzoic acids; and finally Remsen in 1874 (*Annalen*, **178**, 288) prepared another nitrosulphobenzoic acid by heating parasulphaminebenzoic acid with a mixture of nitric and sulphuric acids. To extend our knowledge of these acids, and in particular to determine the orientation of their substituted radicles, is the object of the experiments described in the present paper.

METANITROPARASULPHOBENZOIC ACID, $C_6H_3(COOH)(NO_2)(SO_3H)$.—This, which is the acid discovered by Remsen, was prepared according to his directions, excepting that parasulphobenzoic acid (obtained by treating a solution of toluene in fuming sulphuric acid with potassium permanganate) was used as the starting point instead of parasulphaminebenzoic acid. It crystallises from water, in which it is very soluble, in short thick prisms, containing $2H_2O$, and melting at $130-131^\circ$; dissolves very sparingly in alcohol, and is nearly insoluble in ether, chloroform, and carbon bisulphide. The normal barium salt, $C_6H_3(NO_2)<\overset{CO_2}{SO_3}>Ba + 4H_2O$ (air-dried), is the salt described by

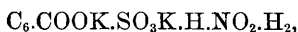
Remsen, who however assigned to it only $1\frac{1}{2}$ mols. H_2O , probably because he dried it over sulphuric acid. It crystallises in concentric groups of yellow needles, moderately soluble in cold, easily in hot water. The *acid barium salt*, $[\text{C}_6\text{H}_3(\text{NO}_2)(\text{COOH})\cdot\text{SO}_3]_2\text{Ba} + 6\text{H}_2\text{O}$, crystallises in long prismatic nearly white needles, which give off 3 mols. water over sulphuric acid. Its solutions show a marked tendency to creep up the sides of the vessel. The *calcium salt*, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{COO})(\text{SO}_3)\text{Ca} + 5\text{H}_2\text{O}$, forms large efflorescent prismatic crystals, having a slightly yellowish colour and moderately soluble in water. The *copper salt*, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{COO})(\text{SO}_3)\text{Cu} + 5\text{H}_2\text{O}$, forms small hard bluish-white crystals. The *normal potassium salt* crystallises in small hard prisms, very soluble in water; the *acid potassium salt*, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{COOH})\cdot\text{SO}_3\text{K} + 1\frac{1}{2}\text{H}_2\text{O}$, in long silky needles, moderately soluble in water, or by slow evaporation in six-sided plates. The *silver salt* is easily soluble in water, and crystallises in large yellowish prisms.

Metamidoparasulphobenzoic acid, prepared by reduction of the preceding acid, and purified by converting it into the barium salt, filtering through animal charcoal, and reprecipitating with hydrochloric acid, forms a white powder, which, when precipitated from a hot, not too concentrated solution, takes the form of warty masses, with a slight tendency to crystallise. It is but sparingly soluble in water even at the boiling heat, nearly insoluble in alcohol, ether, and carbon bisulphide. When heated on platinum foil, it blackens, and gives off fumes having the odour of sulphurous oxide. It appears to be identical with one of the acids which Griess obtained from metamido-benzoic acid. (See page 1144.)

The *normal barium salt*, $\text{C}_6\text{H}_3(\text{NH}_2)(\text{COO})(\text{SO}_3)\text{Ba} + 3\text{H}_2\text{O}$, crystallises in well-formed sharply pointed highly lustrous crystals. Its solution decomposes when evaporated, or even if left to itself for a long time, becoming dirty-brown or yellow, and yielding crystals which are almost black. The colouring matter may, however, be removed by filtration through animal charcoal, and the solutions then show a marked blue fluorescence.

PARANITRO-ORTHOSULPHOBENZOIC ACID, $\text{C}_6\text{H}_3(\overset{1}{\text{COOH}})(\overset{2}{\text{SO}_3\text{H}})(\overset{4}{\text{NO}_2})$, is formed by the action of potassium permanganate on the calcium salt of the nitrotoluenesulphonic acid resulting from the action of sulphuric acid on paranitrotoluene, which has been shown by Ascher (this Journal, 1871, 827) to have the constitution of paranitrotoluenesulphonic acid, $\text{C}_6\text{H}_3\text{CH}_3\cdot\text{SO}_3\text{H}\cdot\text{H}\cdot\text{NO}_2\cdot\text{H}_2$, inasmuch as by converting it into the corresponding amido-acid, replacing the NH_2 -group therein by hydrogen by means of Griess's reaction, and fusing the resulting toluenesulphonic acid with potash, salicylic acid is obtained: whence it follows that the sulpho-group in the sulphonic acid must occupy the ortho-position relatively to the CH_3 .

Normal potassium paranitro-orthosulphobenzoate,



the immediate product of the oxidation of calcium *p*-nitrotoluenesulphonate with potassium permanganate, is anhydrous, and crys-

tallises in groups of short thick opaque prisms, mostly having a faint yellow colour. The *acid potassium salt*, $C_6H_3(COOH)(SO_3K).NO_2 + H_2O$, prepared by adding hydrochloric acid to a strong solution of the normal salt, crystallises in long slender white needles, only moderately soluble in cold water; by slow evaporation of a saturated solution, it may be obtained in thick short transparent prisms. The *barium salt*, $C_6H_3(NO_2) < \begin{smallmatrix} CO_2 \\ SO_3 \end{smallmatrix} > Ba$, is obtained in small compact nearly insoluble crystals on adding barium chloride to a hot moderately strong solution of the potassium salt. On evaporating a saturated solution over a free flame, the salt separates in very delicate micaceous plates, having a fine pearly lustre, and containing in the air-dried state about 4 per cent. water, part of which they lose at a low temperature; the rest above 200° . The compact salt contains about 3 per cent. water. The *calcium* and *copper salts* are very soluble, the former crystallising in prisms, the latter in fine blue needles.

Paramido-orthosulphobenzoic acid, $C_6.COOH.SO_3H.H.NH_2.H_2$, prepared by treating the potassium salt of the nitro-acid just described with ammonium sulphide, evaporating to dryness, and adding hydrochloric acid to the filtered solution, forms long delicate needles, very slightly soluble in cold, more readily in boiling water, nearly insoluble in alcohol and ether. Solutions of the free acid do not become coloured by evaporation; but when rendered neutral or alkaline, they begin to decompose if kept hot, and assume a dirty-brown or black colour. The *barium salt*, $C_6H_3(NH_2)(COO)(SO_3)Ba + H_2O$, crystallises in groups of very slender needles, or by rapid evaporation in mica-like plates; it is but sparingly soluble in water.

ORTHONITROPARASULPHOBENZOIC ACID, $C_6.COOH.NO_2.H.SO_3H.H_2$, is prepared by treating *o*-nitrotoluene with fuming sulphuric acid, neutralising with chalk, evaporating the filtrate to a small bulk, and oxidising the product with potassium permanganate. On neutralising the filtered liquid with hydrochloric acid, evaporating to a small bulk, and then adding hydrochloric acid in excess, a precipitate is formed consisting of the *acid potassium salt*, $C_6H_3(NO_2)(COOH).SO_3K$ which, when purified by recrystallisation, forms anhydrous prismatic plates moderately soluble in hot, less in cold water. The *barium salt*, $C_6H_3(NO_2)(COO)(SO_3)Ba + 2H_2O$, obtained by precipitation, forms small granular yellowish crystals, slightly soluble in cold, more freely in boiling water.

Orthoamidoparasulphobenzoic acid, prepared from the nitro-acid by the action of ammonium sulphide on the potassium salt of the latter, and precipitated from a strong solution of its salts by hydrochloric acid, crystallises in beautiful yellowish rhombic plates, moderately soluble in hot, slightly in cold water and in alcohol, nearly insoluble in ether and in chloroform. Dilute solutions of the acid and of the barium salt show a beautiful blue fluorescence.

As only two amidoparasulphobenzoic acids (and the corresponding nitro-acids) are possible, viz., those in which the orientation is $COOH : NH_2 : SO_3H = 1 : 2 : 4$ and $1 : 3 : 4$, and as the one just described must, according to its mode of formation, be represented by

the second of these formulæ, it follows that the isomeric acid described at page 1145 must be represented by the first—in other words, that it must be metamidoparasulphobenzoic acid. H. W.

Ethylphthalic Acid. By A. MICHAEL (*Am. Chem. J.*, **1**, 413—416).—This compound may be prepared by heating equal parts of absolute alcohol and phthalic anhydride in a reflux apparatus at 100° for ten hours; but the conversion is never complete, even if the heating be prolonged, and the proportion of alcohol to anhydride greatly increased. On evaporating the excess of alcohol at a low temperature, dissolving the residue in water, and neutralising it in the cold with barium carbonate, a mixture of the barium salts of phthalic and ethylphthalic acids is obtained; these may be separated by their different degrees of solubility in water, the precipitate formed on neutralisation consisting for the most part of the less soluble phthalate, while the ethylphthalate, which is extremely soluble in moderately warm water, remains dissolved: by filtering, evaporating to a small bulk, again filtering, and repeating these operations, if necessary, the two barium salts may be easily separated. The filtrate on cooling yields the ethylphthalate, $(\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COO})_2\text{Ba}$, in concentric groups of long white needles, very soluble in cold, and soluble in all proportions in warm water.

The *silver salt*, $\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COOAg}$, obtained by precipitating the aqueous barium salt with silver nitrate, crystallises from water in long needles, which blacken quickly on exposure to light, and are moderately soluble in cold, freely in warm water.

Ethylphthalic acid, $\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, obtained by decomposing the barium salt with sulphuric acid and evaporating in a vacuum, is a heavy oil, moderately soluble in water, decomposed by heat, gradually even at 100° , into ethyl alcohol and phthalic anhydride.

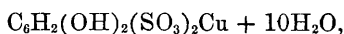
When ethylphthalic acid is gently heated with trichloride or pentachloride of phosphorus, and the product is treated with cold water, a heavy oil is obtained, free from chlorine, and consisting of diethylic phthalate. The first product of the reaction is probably ethylphthalic chloride, $\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$, which then splits up into phthalic anhydride, $\text{C}_6\text{H}_4 \cdot \text{C}_2\text{O}_2 \cdot \text{O}$, and ethyl chloride, and the latter acts on unchanged ethylphthalic acid, with formation of hydrochloric acid and diethylic phthalate, $(\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH} + \text{EtCl} = \text{HCl} + \text{C}_6\text{H}_4(\text{COOEt})_2$. H. W.

Resorcinolsulphonates. By H. FISCHER (*Monatsh. Chem.*, **2**, 331—344).—Resorcinoldisulphonic acid is formed by adding 1 pt. finely pulverised resorcinol, with constant stirring, to 4 pts. sulphuric acid at ordinary temperature, the syrupy liquid after a while becoming heated to 90° , and solidifying to a compact crystalline pulp, which must be freed from excess of acid by draining on porous tiles. On dissolving the hygroscopic residue in warm water, saturating with levigated barium carbonate, filtering the liquid while hot, and concentrating it on the water-bath, *normal barium resorcinoldisulphonate*, $\text{C}_6\text{H}_2(\text{OH})_2(\text{SO}_3)_2\text{Ba} + \frac{3}{2}\text{H}_2\text{O}$, separates in nearly colourless monoclinic crystals, which are permanent in the air, and easily soluble in

hot water. On mixing its dilute solution with barium hydroxide, the insoluble *basic salt*, $C_6H_2(O_2Ba)(SO_3)_2Ba + 4H_2O$, described by Piccard and Humbert (this Journal, 1877, 1, 312), separates after a short time in needles having a satiny lustre.

Potassium resorcinoldisulphonate, $C_6H_2(OH)_2(SO_3K)_2$, is obtained from the barium salt by double decomposition with potassium sulphate, and crystallises with 1 and with 4 mols. H_2O . The monohydrate separates from a hot saturated solution on cooling in colourless monoclinic prisms, easily soluble in warm water, and permanent in the air. The tetrahydrate, which crystallises from cold solutions, is efflorescent, and on exposure to dry air gives off 13 per cent., or 3 mols. water.

The *sodium salt*, $C_6H_2(OH)_2(SO_3Na)_2 + H_2O$, prepared like the potassium salt, forms monoclinic twinned crystals, which resemble the monohydrated potassium salt in colour, and in solubility in warm water, and are likewise permanent in the air.—The *copper salt*,



prepared in like manner, forms triclinic crystals, having the colour of cupric chloride, giving off part of their water on exposure to the air at ordinary temperatures, and decomposing at 170° , without giving up the rest of the water.—A *basic lead salt*, $C_6H_2(O_2Pb)(SO_3)_2Pb + 4H_2O$, is formed on mixing the hot solutions of the potassium salt and normal lead acetate, and crystallises on cooling in fine colourless scales; it is then insoluble in water, and may be obtained quite pure by washing therewith. The concentrated mother-liquor contains,—together with unaltered potassium salt,—potassium acetate and free acetic acid, which retains in solution a portion of the lead salt, and deposits it on careful neutralisation with potassium carbonate.

Action of Caustic Alkalis on Resorcinoldisulphonates.—When 1 pt. potassium resorcinoldisulphonate is heated with 4 pts. potassium hydroxide, till a brisk evolution of hydrogen takes place, and the operation is interrupted as soon as the frothing ceases, the lixiviated melt is found to contain the potassium salt of resorcinolmonosulphonic acid, together with sulphate and undecomposed disulphonate. To separate these salts, the free alkali is neutralised with acetic acid, the undecomposed resorcinoldisulphonic acid and the sulphurous acid are removed by means of a slight excess of baryta, which under these circumstances does not precipitate the monosulphonic acid; and the liquid, after being filtered and warmed, is freed from excess of baryta by carbonic acid, and finally treated with basic lead acetate, which completely throws down the basic lead salt of resorcinolmonosulphonic acid. The precipitate, after washing with warm water, is decomposed by hydrogen sulphide; the filtered solution is saturated with potassium carbonate, and evaporated on the water-bath to complete dryness; and the residue, intimately mixed with sand, is digested with absolute alcohol, to extract the potassium resorcinol-sulphonate, which, by evaporation of the alcohol, and once recrystallising from water, is obtained quite pure.—*Potassium resorcinolmonosulphonate*, $C_6H_2(OH)_2.SO_3K + 2H_2O$, crystallises in faintly yellow monoclinic prisms, which give off part of their water in dry air, the rest at 170° . Its aqueous solution

is not precipitated by normal lead acetate, barium acetate, or barium hydroxide.

If, on the other hand, instead of stopping the action of the alkali on the resorcinoldisulphonate just as the frothing ceases—that is to say just as the formation of the monosulphonate takes place—the fusion be prolonged at a higher temperature till the mass assumes a yellow-brown colour, and the cooled melt be then dissolved in water and acidulated with sulphuric acid, the filtered solution shaken up with ether, and the ether left to evaporate, there remains a crystallised body, exhibiting the melting point and all the other characters of phloroglucinol. A similar reaction takes place when sodium resorcinoldisulphonate is fused with sodium hydroxide, but the yield of phloroglucinol is then much smaller.

Action of Iodine on Resorcinolsulphonates.—The iodation of potassium resorcinoldisulphonate is best effected by intimately triturating 1 mol. of the salt with 2 mols. iodine (30 g. salt to 22 g. iodine), introducing the mixture into a bottle, which can be tightly closed, and digesting it in the water-bath for 6 hours with 200–300 c.c. of a mixture of equal volumes of water and alcohol. On cooling, the iodised product separates in crystals, mixed with free iodine, which may be removed by treatment with ether alcohol; and on dissolving the residue in hot water, and leaving the solution to cool, *potassium iodoresorcinoldisulphonate*, $C_6HI(OH)_2(SO_3K)_2$, separates in colourless, anhydrous crystals, often a centimeter long.

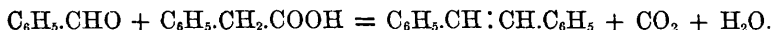
Potassium iodoresorcinolmonosulphonate, $C_6H_2I(OH)_2.SO_3K + 3H_2O$, is prepared in a similar manner, but is very difficult to purify, on account of its great solubility in water and in dilute alcohol, the syrupy solution depositing crystals only with great difficulty. The pure product forms white microscopic crystals, which may be heated to 150° without decomposition.

Action of Potassium Nitrite on Potassium Resorcinoldisulphonate.—When a solution of potassium resorcinoldisulphonate, saturated in the cold, is mixed with potassium nitrite, it soon acquires a pale violet, and afterwards a darker colour, without yielding any deposit; but on adding a few drops of acetic acid to the mixture, a slow evolution of gas takes place, and after some time a dark violet potassium salt separates in well-defined crystals. This salt is nitrogenous, and retains the two SO_3 -groups intact. It dissolves in hot more readily than in cold water; detonates when quickly heated; gives up part of its potassium to strong hydrochloric or dilute sulphuric acid; and when placed over sulphuric acid, loses 9 per cent. water, which it recovers on exposure to the air. The violet solution is decolorised by reducing agents, and gives with mercurous nitrite a black precipitate, flocculent at first, but afterwards becoming crystalline, and with cupric chloride a crystalline precipitate, slightly soluble in cold, more readily in hot water, with ferric chloride an emerald-green solution. This salt gave by analysis 15.42–15.59 per cent. C, 2.13–2.25 H, 13.47 S, 3.21–4.19 N, 24.34–24.55 K, and 19.92–13.14 H_2O . On heating its cold saturated solution with strong hydrochloric acid mixed with an equal volume of absolute alcohol, another salt is obtained in highly lustrous

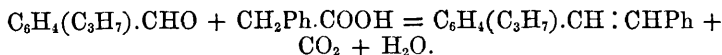
scales, containing 18.52—18.64 per cent. K, 15.49—15.69 S, and 75.5—8.06 H₂O. A nitrogenous barium salt is likewise obtained by the action of barium nitrite on barium resorcinoldisulphonate in presence of acetic acid. Lastly, potassium resorcinolmonosulphonate, treated with potassium nitrite and acetic acid, yields a salt which crystallises in light green needles, having a silky lustre. No definite formulæ have yet been obtained for any of these salts. H. W.

A New Formation of Stilbene and some of its Derivatives.

By A. MICHAEL (*Am. Chem. J.*, 1, 312—316). The reaction in question is similar to that by which Perkin effected the synthesis of cinnamic acid and its homologues (this Journal, 1877, i, 389), and consists in heating together in sealed tubes equivalent quantities of benzaldehyde and phenylacetic acid—or substitution-derivatives of these bodies, and anhydrous sodium acetate. When benzaldehyde and phenylacetic acid are thus heated together for 12 hours, at 250°, considerable quantities of carbonic anhydride escape on opening the tube; and on extracting the contents of the tube, first with boiling water, and then with warm dilute ammonia, to remove traces of unchanged phenylacetic acid, treating the undissolved residue which melts under warm water, with animal charcoal, and finally crystallising it several times from alcohol, a product is obtained, having the composition and properties of stilbene, C₁₄H₁₂, and amounting to between 50 and 60 per cent. of the theoretical quantity. Its formation is represented by the equation—

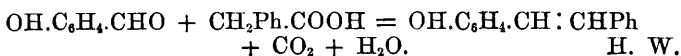


A mixture of equal parts of cumic aldehyde and phenylacetic acid, heated with about one-third part of anhydrous sodium acetate for about 15 hours at 250°, yields in like manner *isopropylstilbene*, C₁₇H₁₈, as shown by the equation—



The product after purification by repeated treatment in alcoholic solution with animal charcoal, and three recrystallisations from hot alcohol, was obtained in cauliflower-like groups of fine glittering crystalline scales. It is insoluble in cold, and very slightly soluble in warm water; melts at 83—84°, and solidifies on cooling. It forms an addition-product with bromine.

When *salicylaldehyde* and phenylacetic acid are heated in like manner with sodium acetate for about 12 hours at 200°, a very complicated reaction takes place, giving rise to a large quantity of resinous matter, from which by extraction with boiling water, dilute ammonia, and hot alcohol, a small quantity of a crystalline substance is obtained, having the composition C₁₄H₁₂O, and regarded by the author as *orthohydroxystilbene*, its formation being represented by the equation—



H. W.

Preparation of Pure Naphthalene. By G. LUNGE (*Chem. News*, **44**, 65).—Crude naphthalene is heated with 5–10 per cent. sulphuric acid of 170 Tw., and then 5 per cent. manganese dioxide is added, and the mixture heated on a water-bath until all action ceases. The acid is drawn off, and the naphthalene washed, first with water, then with weak sodium hydrate solution, and finally with water. The naphthalene is then distilled, and will remain permanently white. Manganese dioxide may be replaced by other oxidising agents, but probably none will be found cheaper. C. H. B.

Essence of Erigeron Canadense. By F. VIGIER and C. CLOEZ (*J. Pharm. Chim.* [5], **4**, 236–241).—*Erigeron canadense* frequently grows in the mint fields of America, and its essence is one of the most common impurities in American peppermint oil. No method of detecting it, when mixed with peppermint oil, is yet known. Commercial essence of mint varies greatly in composition, specific gravity, and molecular rotatory power. C. H. B.

Phytolacca Dioïca. By BALLANT (*J. Pharm. Chim.* [5], **4**, 232–234).—*Phytolacca dioïca*, according to De Candolle, is indigenous to Brazil or Mexico. In Paris it is known only as a greenhouse shrub, but it flourishes on the Algerian coast. Its wood is very spongy and fibrous, and never acquires a true ligneous structure. The fruit is a fleshy greenish-yellow berry, forming grape-like clusters weighing from 30 to 40 grams. It falls off naturally about October, and is then very sweet. When pressed it yields about 74 per cent. of a thick, gummy, slightly acid syrup, with a somewhat nauseous odour. Sp. gr. = 1.100. This syrup does not ferment spontaneously, and clarifies very slowly when exposed to the air. After filtration it has a brown colour, and its dilute aqueous solution is distinctly fluorescent. The syrup contains 24.6 per cent. solid matter, which, on ignition, leaves 1.86 per cent. ash. It has the composition—

Water	75.40
Chlorophyll, wax, resin, essential oil, and volatile acid	0.45
Sugar, reducing	3.20
Sugar, non-reducing	11.20
Organic acid (not determined)	2.60
Gum	4.40
Albuminoid matters, pectic substances, and pectose ..	0.89
Inorganic salts	1.86
	<hr/>
	100.00

The resin, which, like the essential oil to which the syrup owes its peculiar odour, exists only in very small quantity; is very bitter, and is insoluble in ether. The ethereal salt of the volatile acid has an odour recalling that of ethyl butyrate. The undetermined organic acid exists as a potassium salt, which does not crystallise, and dissolves in water, but is insoluble in ether. Its solution gives no precipitate with barium nitrate; it therefore has some of the properties of the phyto-

laccic acid extracted by Terreil from the fruit of *Phytolacca decandra*. The ash consists mainly of potassium carbonate, with small quantities of iron, calcium, magnesium, silica, and phosphoric acid, and traces of sulphuric acid and chlorine. No alkaloid was obtained from the syrup.

C. H. B.

Aspidium Rigidum. By W. J. BOWMAN (*Pharm. J. Trans.* [3], 12, 263—264).—The rhizome of this fern contains a resin similar to that obtained by Luck from *Aspidium filix mas*, filicic acid, fat, tannin, glucose, gum, pectin, and starch.

C. H. B.

Quebrachitannic Acid. By P. N. ARATA (*Anales de la Sociedad Científica Argentina*, Febrero, 1879).—This acid is obtained from the so-called "gum" of the *Quebracho colorado*, formerly called *Loxopterygium Lorentzii*, but now referred by Grisebach to a distinct genus, and called *Quebrachia Lorentzii* (see this Journal, 1878, Abstr., 986). It may be prepared from the wood or from the gum of the tree by various processes, best, however, by dissolving the gum, previously purified by treatment with alcohol, in boiling water, and filtering hot, the filtered liquid as it cools depositing a tannin in reddish tufts, which must be washed rapidly on a filter, pressed between bibulous paper, and dried over sulphuric acid. The mother-liquor still, however, retains a considerable quantity of the tannin, which may be separated by treating the solution with hydrochloric acid, sulphuric acid, or common salt: when washed and dried as above described, it constitutes nearly pure quebrachitannic acid. In whatever manner the acid may be prepared, it is very apt to become coloured by contact with the air or with alkalis, and even by prolonged boiling of its solutions: moreover, the colour thus produced cannot be removed by means of animal charcoal, which, on the contrary, gives rise to the formation of products having a deeper colour and resinous aspect.

Quebrachitannic acid is a pale-red amorphous mass, having an astringent taste, and yielding a light cinnamon-coloured powder. It is insoluble in carbon bisulphide, chloroform, turpentine-oil, and benzene. Its aqueous solution is precipitated by various metallic salts; with lead acetate, normal or basic, a white precipitate is formed which, when heated, acquires, first a rose and then a chocolate colour; with ferric chloride a green liquor is produced, changing, after a while, to dark-red, and becoming black on addition of sodium acetate. With gelatin, albumin (either of egg or of blood), and solutions of the alkaloids, white precipitates are formed.

Quebrachitannic acid is decomposed by dry distillation, yielding catechol. Strong nitric acid converts it into oxalic and picric acids. By fusion with potassium hydroxide, it is resolved into phloroglucol and protocatechuic acid, and the same products are formed by the action of sulphuric acid on its aqueous solution.

The above-described properties show that quebrachitannic acid belongs to the group of tannins which precipitate gelatin and colour ferric salts green, like catechutannic and kinotannic acids: but it does not agree exactly in composition with either of these acids, as the following comparison will show:—

	Carbon.	Hydrogen.
Catechutannic acid.....	62.06	4.43
Kinotannic acid	62.91	4.48
Quebrachitannic acid	52.52	5.11

Neither does it agree exactly in composition or properties with any of the other tannins which give green precipitates with ferric salts: hence the author regards it as a distinct chemical species.

Quebrachicatechin.—This body, the existence of which in quebracho gum was rendered probable by the author's former experiments, may be prepared by dissolving the gum (about 1 kilo.) in boiling water, precipitating the quebrachitannic acid with sulphuric acid; agitating the filtered liquid with twice its volume of ether; distilling off two-thirds of the ether; then evaporating to dryness, and treating the residue with dilute alcohol, which dissolves the crystals that have formed, leaving a resinous substance undissolved; and on treating the solution with a small quantity of basic lead acetate to precipitate the quebrachitannic acid dissolved by the ether, evaporating the filtrate on the water-bath, and leaving it at rest, a yellowish crystalline mass is obtained, the alcoholic solution of which leaves the catechin on evaporation in yellowish crystals.

Quebrachicatechin is insoluble in cold, and only slightly soluble in hot water; very soluble in alcohol and ether. Its solution is clouded by normal lead acetate; gives rose-coloured precipitates with basic lead acetate and with mercurous nitrate, blackish with a mixture of ferrous sulphate and sodium acetate; reduces silver nitrate and gold chloride; is coloured yellow by nitric acid, red by sulphuric acid, yellowish by sodium hypochlorite, green by Fehling's solution; does not precipitate gelatin or the alkaloids.

The quantity of quebrachicatechin obtained was not sufficient for analysis, but from its reactions and its analogy to other members of the catechin group, the author infers that it stands to quebrachitannic acid in the relation of acid to anhydride. H. W.

Spigeline, a New Volatile Alkaloid. By W. L. DUDLEY (*Am. Chem. J.*, 1, 138).—This alkaloid is obtained from *Spigelia marilandica*, or pink-root,—a plant which has long been known to possess peculiar medicinal properties,—by distilling the ground root with milk of lime. The distillate is collected in a receiver containing hydrochloric acid, the solution evaporated to dryness over a water-bath, the residue exhausted with absolute alcohol, and the filtered solution left to evaporate. A small quantity of a crystalline substance then remains, which is soluble in water and gives with potassio-mercuric iodide a white crystalline precipitate, soluble in acids, alcohol, and ether, but insoluble in excess of the precipitant; by this reaction, spigeline is distinguished from the other volatile alkaloids, nicotine, conine, and lobeline, which give yellow precipitates with potassio-mercuric iodide. Spigeline also gives a white precipitate with metatungstic acid. H. W.

Methyl-ether of Morphine. By O. HESSE (*Pharm. J. Trans.* [3], 12, 157).—The product of the action of methyl iodide on an alcoholic

solution of morphine and potassium hydroxide is not codeine, but an isomeride, *β-methyl-morphine*, an amorphous substance soluble in water, giving a solution with a strongly alkaline reaction; readily soluble in ether, chloroform, and methyl and ethyl alcohols. *β-Methyl-morphine hydrochloride* has the composition $C_{17}H_{18}MeNO_3, HCl + 2H_2O$, crystallises in long silky needles, which lose their water at 100° , and dissolve in 10.8 parts of water at 18° . The solution gives no reaction with ferric chloride, but a flocculent precipitate with platinum tetrachloride, somewhat soluble in water. A saturated solution becomes milky on adding potassium hydroxide or strong ammonia, and finally deposits an amorphous precipitate. The molecular rotatory power of the compound is $[\alpha]_D = -108.19$. Codeine hydrochloride has the same composition and rotatory power, and gives the same reactions with ferric chloride and platinum tetrachloride, but it crystallises in short white prisms, which lose only $\frac{1}{2}$ mol. H_2O at 100° , the remainder being given off above 120° . It dissolves in 23.8 parts of water at 18° , and a saturated solution deposits a crystalline precipitate on addition of an alkali. When sodium hydroxide is substituted for potassium hydroxide, about half the product consists of *β-methyl-morphine*, the other half being an alkaloid, having a great similarity to codeine, but the rotatory power of its hydrochloride is $[\alpha]_D = -104.8$, whilst that of codeine hydrochloride is $[\alpha]_D = -108.1$. The author considers that there is no proof that the codeine extracted from opium and that obtained by the action of methyl iodide on morphine are identical (Grimaux, this vol., 829). He objects to the application of the generic term "codeine" to compounds which are simply ethers of morphine.

C. H. B.

Quinoïdine Borate, a New Febrifuge. By J DE VRIJ (*J. Pharm. Chim.* [5], 4, 234—236).—Cinchona bark contains, as is well known, an amorphous alkaloid, quinoïdine, which in some cases amounts to as much as 30 per cent. of the total quantity of alkaloids extracted from the bark. The compounds of quinoïdine, which is a valuable febrifuge, are all amorphous, and very soluble in water, consequently this alkaloid is found in the mother-liquors from the manufacture of quinine sulphate. On adding an alkali it is precipitated, together with a large quantity of impurities, in the form of a dark-coloured resinous mass. The author has been able to isolate the alkaloid in a state of purity by combining it with boric acid. Quinoïdine borate is a yellowish, amorphous, very slightly deliquescent powder, soluble in three parts of water, giving a solution with a distinctly alkaline reaction. Its much greater solubility renders it superior to quinine for hypodermic injections. The salt contains 54 per cent. of quinoïdine, and has a molecular rotatory power, varying between $+10^\circ$ and $+20^\circ$. In the treatment of ordinary fevers, 1 gram quinoïdine borate gives the same result as 0.666 gram quinine sulphate. The new febrifuge costs about 40 francs per kilo.

C. H. B.

Conquinamine. By A. C. OUDEMANS (*Annalen*, 209, 38—61).—A continuation of the author's researches on the alkaloids of the "quinetum of Darjeeling" (Abstr., 1879, 1044). In order to separate

conquinamine and quinamine from the crude products; the quinine and cinchonidine are removed by precipitation as tartrates, and the filtrate precipitated by potassium hydroxide. This precipitate is boiled with 50 per cent. alcohol, and from the filtered liquid there separates on cooling a mixture of cinchonine, quinamine, and conquinamine (quinidine may be precipitated as thiocyanate from the filtrate from this mixed precipitate). These mixed alkaloids are shaken up with ether to remove the cinchonine, and the residue is dissolved and subsequently recrystallised slowly from 60 per cent. alcohol. The crystals are then separated by a fine metallic sieve which retains the larger crystals of the conquinamine. Quinamine and conquinamine, however, are better separated from one another by fractional crystallisation of their nitrates, oxalates, or hydrobromides, these conquinamine salts being less soluble than those of quinamine. Pure conquinamine is obtained by precipitating the nitrate with caustic soda, dissolving the precipitated alkaloid in alcohol, and recrystallising.

Conquinamine forms colourless to golden-yellow transparent crystals of the tetragonal system (m. p. 123°), easily soluble in alcohol, ether, benzene, and chloroform, sparingly soluble in water. The specific rotatory power was determined in various solutions of the alkaloid in alcohol, ether, chloroform, and benzene.

Solvent.	Conquinamine in 100 c.c.	$[\alpha]_D$.
Absolute alcohol	{ 0.8025 grams	+ 205.1
	{ 2.7115 "	202.6
	{ 4.0180 "	204.1
Ether	{ 0.7655 "	192.7
	{ 1.6115 "	189.0
	{ 4.6460 "	190.3
Chloroform	{ 0.7945 "	176.1
	{ 1.5310 "	173.8
	{ 3.0500 "	171.2
Benzene	{ 0.8955 "	180.1
	{ 2.1285 "	178.6
	{ 3.4470 "	178.0

From these results it appears that the specific rotatory power of conquinamine in alcoholic and ethereal solution, at first decreases with greater concentration, but subsequently increases.

The results of analyses agree with the formula $C_{19}H_{24}N_2O_2$, assigned to conquinamine by Hesse.

The reactions of conquinamine with platinic chloride, sulphuric and nitric acids, and the higher acids of chlorine, resemble those of quinamine.

Conquinamine sulphate, $(C_{19}H_{24}N_2O_2)_2 \cdot H_2SO_4 + xAq$, is very soluble in water; it is obtained from alcoholic solution in slender needles.

Conquinamine hydrochloride, $C_{19}H_{24}N_2O_2 \cdot HCl + xAq$, is very soluble in water; on evaporation, it separates out as an amorphous mass, with signs of crystallisation.

Conquinamine hydrobromide, $C_{19}H_{24}N_2O_2 \cdot HBr$, crystallises in monoclinic crystals of combination ∞P : $-P$: $\infty P\infty$. Specific rotation of a

solution of salt in alcohol (1.162 grams in 100 c.c.) $[\alpha]_D = + 182.7$, and of the alkaloid in the form of hydrobromide $[\alpha]_D = + 228.1$.

Conquinamine hydriodide, $C_{19}H_{24}N_2O_2 \cdot HI$, crystallises in leaflets. Specific rotation of salt in alcohol (1.011 gram in 100 c.c.) $[\alpha]_D = + 162.8$, and of the alkaloid in the form of hydriodide $[\alpha]_D = + 229.5$.

Conquinamine nitrate, $C_{19}H_{24}N_2O_2 \cdot HNO_3$, crystallises in the rhombic system. Combination $OP : P$. Specific rotation of salt in alcohol (1.2685 gram in 100 c.c.) $[\alpha]_D = + 190$, and of the alkaloid in the form of nitrate $[\alpha]_D = + 228.6$.

Conquinamine chlorate, $C_{19}H_{24}N_2O_2 \cdot HClO_3$, crystallises in monoclinic needles. Specific rotation of salt in alcohol (.9150 gram in 100 c.c.) $[\alpha]_D = + 184$, and of the alkaloid as chlorate $= + 234$.

Conquinamine perchlorate, $C_{19}H_{24}N_2O_2 \cdot HClO_4$, crystallises in long needles of the monoclinic system. Specific rotation of salt in alcoholic solution (.71 gram in 100 c.c.) $[\alpha]_D = + 175.4$, and of the alkaloid as perchlorate $[\alpha]_D = + 231.4$.

Conquinamine platinochloride, $(C_{19}H_{24}N_2O_2 \cdot HCl)_2 \cdot PtCl_4 + 3H_2O$, forms an orange-golden amorphous precipitate, which is slowly decomposed by water forming a rose-coloured solution.

Conquinamine formate crystallises in the monoclinic system, the *acetate* in the tetragonal, and the *oxalate* in the rhombic system. On heating this last salt to 115° it darkens, and on dissolving the mass in acidified water, and precipitating with soda, a compound, differing from the original conquinamine, is thrown down (probably the apoquinamine of Hesse).

The author has studied the influence of excess of various acids on the specific rotatory power of conquinamine, and has arrived at results similar to those obtained with quinamine (cf. *supra*), viz., that the specific rotatory power reaches its maximum when 1 mol. of a monobasic, or $\frac{1}{2}$ mol. of a bibasic acid is added to 1 mol. of the alkaloid. Therefore the alkaloid, like quinamine, is monobasic. It also appears probable that, as the specific rotatory powers of the alkaloid existing as salts of organic acids do not agree with those of the salts of the inorganic acids, the organic acid salts are partially decomposed in solution.

V. H. V.

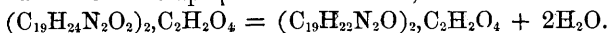
Conquinamine. By O. HESSE (*Annalen*, 209, 62—69).—The author has previously observed in the alcoholic mother-liquor obtained in working up the barks of the *Cinchona succirubra*, the presence of an alkaloid, *Conquinamine* (cf. this vol., 923). The method of separating this alkaloid does not essentially differ from that adopted by Oudemans (see preceding Abstract). The pure alkaloid is obtained by precipitating the nitrate with ammonia, and is purified by recrystallisation from 60 per cent. alcohol. It crystallises in tough prisms (m. p. 121°). The analyses agree with the formula $C_{19}H_{24}N_2O_2$. On heating with hydrochloric acid (sp. gr. $= 1.125$) it is decomposed into apoquinamine and water, thus: $C_{19}H_{24}N_2O_2 = C_{19}H_{22}N_2O + H_2O$. Conquinamine resembles quinamine in all its chemical properties.

Conquinamine Hydrochloride.—Contrary to the observation of Oudemans, the hydrochloride may be obtained in octohedral crystals:

on precipitating an aqueous solution of this salt with sodium platinum-chloride, a golden flocculent precipitate is thrown down of the *platino-chloride* of the alkaloid $(C_{19}H_{24}N_2O_2)_2 \cdot PtCl_6H_2 + 2H_2O$. With auric chloride, the hydrochloride gives a golden precipitate, which rapidly becomes purple; mercuric chloride and potassio-mercuric iodide form white flocculent precipitates.

Conquinamine quinate, $C_{19}H_{24}N_2O_2 \cdot C_7H_{12}O_6 + 2H_2O$, crystallises in long colourless prisms, easily soluble in alcohol and water.

The *neutral oxalate* when heated to 105° is converted first into quin-amicine and then into apoquinamine oxalate, thus:



The author made the following observations of the rotatory power of conquinamine ($t = 15$):—

P.	Solvent.	$[\alpha]_D$.
2	97 per cent. alcohol.....	+ 204.6
2	Chloroform	184.5
2	Water + 1 mol. HCl	229.1
4	Water + 3 mols. HCl....	230.0
4 Conquinamine } hydrochloride }	Water	205.3

The author observes that conquinamine shows the same specific rotatory power in acid as in neutral solutions, but cannot accept Oudemans' view that this phenomenon is correlated with the basicity of the alkaloid. Thus, for instance, hydrochlorapocinchonine has the same specific rotatory power in acid and neutral solutions, but yet is undoubtedly a bi-acid base.

The author also alludes to the fact that the difference of specific rotatory power of quinamidine and quinamine in 97 per cent. alcohol is half as great as that between quinamidine and conquinamine. This fact lends support to the second law of Krecke, recently elaborated by Thomsen (*Ber.*, **13**, 2267). The author arrives at the conclusion that conquinamine and quinamine are two isomeric bases, which cannot however be converted directly one into the other. V. H. V.

Alkamines. By A. LADENBURG (*Compt. rend.*, **93**, 338—340).—The study of tropine has led the author to suppose that it contains an alcoholic hydroxyl group, which gives to it its characteristic property of forming alkaloids on treatment with acids in hydrochloric acid solution. By this means, the author has prepared the tropeïnes, amongst which are atropine and homatropine, and has found a method of preparing a whole class of bases, possessing, like atropine, the property of etherification in hydrochloric acid solution. The ethers so formed resemble in their properties and composition the natural alkaloids. These new bases at the same time possess the function of an alcohol and an amine: hence the author proposes for them the name of *Alkamines*, and for their derived ethers the name *Alkameïnes*. The alkamines are prepared by the action of the chlorhydrins on the secondary amines; they are volatile, well characterised bases.

Piperethylalkamine, $C_7H_{15}NO$, formed by the action of ethylene chlorhydrin on piperidine, is a liquid (b. p. 199°) having a feeble

ammoniacal odour. Its aurochloride (m. p. 129°) crystallises in fine scales, readily soluble in water. By the action of acids in hydrochloric acid solution, it gives alkameïnes, of which the author has only studied that obtained from phenylacetic acid. This alkameïne forms an aurochloride, $C_{15}H_{24}NO_3 \cdot HCl \cdot AuCl_3$, crystallising in fine needles, a platinochloride in scales, and a periodide in silky needles.

Triethylalkamine, $C_6H_{15}NO$, is a limpid liquid (b. p. 160°), soluble in water, and forming soluble salts; with cinnamic acid it gives an alkameïne, which is characterised by a picrate crystallising in soluble needles.

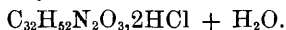
Diallylethylalkamine, $C_8H_{16}NO$, isomeric with tropine, is a liquid (b. p. 197°) sparingly soluble in water, and forming a characteristic picrate.

Dipiperallylalkamine, $C_{10}H_{23}N_2O$, is formed by the action of glycerol chlorhydrin on piperidine. It boils at $280-290^{\circ}$ with slight decomposition, it gives a platinochloride of formula $C_{10}H_{23}N_2O_2 \cdot HCl \cdot PtCl_4$.

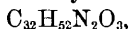
Piperpropylalkamine, C_8H_7NO , prepared from propylenic chlorhydrin, boils at 197° . The author proposes to continue the study of these alkalines and alkameïnes in their chemical and physiological aspects.

V. H. V.

Lycopodine. By K. BÖDEKER (*Annalen*, **208**, 363—367).—An alkaloid can be obtained from *Lycopodium complanatum* by the following process. The dried plant is twice treated with boiling alcohol; and the residue which remains when the alcoholic solution is evaporated is repeatedly extracted with warm water. Basic lead acetate is added to the aqueous solution, the precipitate removed by filtration, and the lead in the filtrate is precipitated by sulphuretted hydrogen. The liquid, after evaporation, is mixed with an excess of alkali and shaken with ether. The ethereal extract is evaporated, and the residue which remains is dissolved in dilute hydrochloric acid. After repeated recrystallisation from water, the hydrochloride is obtained in peculiar monoclinic crystals, which have the composition



With gold chloride it forms a double salt, $C_{32}H_{52}N_2O_3 \cdot 2HCl \cdot 2AuCl_3 + H_2O$, which crystallises in lustrous yellow needles. *Lycopodine*,



is obtained by placing a stick of solid potash in a concentrated solution of the hydrochloride, to which an excess of sodium hydroxide has previously been added. A colourless resin is then deposited, which slowly changes into monoclinic crystals. The alkaloid melts at 114° , and is freely soluble in alcohol, ether, benzene, water, and amyl alcohol. It has a very bitter taste.

W. C. W.

Vicin and Convicin. By H. RITTHAUSEN (*J. pr. Chem.* [2], **24**, 202—220).—The author has already described (*ibid.*, **2**, 336, and **7**, 374) the method of preparation and the properties of vicin, the nitrogenous substance found in *Vicia sativa*. In the present communication, he gives an account of later methods employed. 80 kilos. of the powdered seeds are treated with hydrochloric acid, to which,

after 3—4 hours, milk of lime is added in excess. After standing for some time, the supernatant clear liquid is decanted, and mixed with milk of lime and mercuric chloride, until no further precipitate is formed. This precipitate, after washing, addition of baryta-water, and heating, is decomposed by sulphuretted hydrogen, filtered hot, and the baryta is precipitated by carbonic anhydride. Further evaporation causes the separation of albumin, &c., and finally from the liquid, greatly reduced in bulk, vicin crystallises out, leaving convicin in solution, which separates in brilliant plates, when the liquid is more concentrated. Purification of the vicin is effected by means of 80 per cent. alcohol and charcoal. The yield is only 0.355 per cent. The analyses of the vicin obtained in previous years pointed to the formula $C_8H_{16}N_3O_6$, but those of the more carefully purified substance require $C_{28}H_{51}N_{11}O_{21}$ as the formula. One part of vicin is soluble in 108 of water, and at 120° it loses 2 aq., decomposing at 180° . Lime and baryta-water, as also dilute potash, dissolve vicin without decomposition; the same is the result when hydrochloric and sulphuric acids are employed; but if the temperature is raised to boiling, and the concentration of the acids increased, a yellow solution is formed, which, when cold, is changed to a deep blue on the addition of a small quantity of ferric chloride and ammonia. If baryta-water is used, then a violet-blue precipitate is produced, which loses its colour when boiled, and reduces silver nitrate. The following salts have been prepared: $3(C_{28}H_{51}N_{11}O_{21}) \cdot 4H_2SO_4$ and $4(C_{28}H_{51}N_{11}O_{21}) \cdot 11HCl$; the nitrate could not be obtained, as nitric acid decomposes the base, which however combines with metallic oxides, such as mercuric oxide. Vicin boiled with potash yields ammonia, and gives the same reaction with ferric chloride and ammonia above referred to. If, however, the potash is strong, then decomposition goes too far, and this reaction does not occur. In no case does hydrocyanic acid appear, so long as the potash is in solution; but on fusion, the evolution of ammonia is greater, and on treating the product with sulphuric acid, hydrocyanic acid is evolved; a crystalline substance soluble in ether is formed at the same time. This formation of the hydrocyanic acid should lead to a definite knowledge of the constitution of vicin, but the author is unable to continue the investigation. This same reaction is mentioned in the former paper, and was then ascribed to amygdalin.

Decomposition by Acids.—When vicin is heated with dilute sulphuric acid (1:5), a white crystalline substance separates out, and a gas is evolved; these crystals also show the iron and ammonia reaction. This substance, which is combined with sulphuric acid, has been named *divicin*, $2(C_{11}H_{19}N_{10}O_8) \cdot 5SO_3$, and the pure divicin has also been separated in prismatic crystals, which reduce silver nitrate, and have the composition $C_{31}H_{50}N_{30}O_{16}$. The gas which is evolved is believed to be octyl hydride. Aqueous solutions of divicin decompose on evaporation. Nitric acid transforms divicin into a substance sparingly soluble in water, which appears to be a nitrate, $C_{31}H_{50}N_{30}O_{16} \cdot 8HNO_3$. Fused potash causes the formation of ammonia and potassium cyanide; so that here, as in vicin, nitrogen exists in the two forms of CN and

NH_3 , or NH_2 . The action of sulphuric acid on vicin is therefore principally to produce divicin, but other substances are also formed.

Convicin.—This substance already referred to is separated from vicin by treating the mixture with dilute sulphuric acid, which dissolves the latter readily, but not the former. Convicin crystallises in thin rhombic colourless plates, often aggregated together, resembling leucin. Strong potash-solution does not produce ammonia from convicin; neither have dilute acids any decomposing action. The aqueous solution is precipitated by mercuric nitrate, and other metallic salts also produce precipitates, but only when the solution is neutral. Convicin, $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}_7 \cdot \text{H}_2\text{O}$, melts without decomposition.

E. W. P.

Action of Salt-solutions on Conglutin and Legumin. By H. RUTHAUSEN (*J. pr. Chem.* [2], **24**, 221—225).—Sweet and bitter almonds, and peach-kernels, when deprived of fat, dissolve in a 5 to 10 per cent. solution of common salt, forming liquids which are but slightly or not at all clouded by dilution with a large quantity of water; but the addition of a few drops of acid to these solutions—as to that prepared with distilled water—throws down a considerable quantity of albuminous substance, agreeing in all its properties with that which is obtained from the aqueous solution. When yellow and blue lupines are treated with a 5 per cent. solution of sodium chloride, a solution is obtained which deposits a gliadin-like mass on further dilution. This hardens when washed with water and alcohol. The mother-liquors from which the gliadin has been precipitated also contain a substance precipitable by copper sulphate. The portion insoluble in salt-solution is, however, soluble in potash. This latter conglutin substance seems to possess all its original properties, unaltered by the potash, and is identical with that from earth-nut, but not with that from almonds, hazel-nuts, and peach kernels, and seems to contain twice as much sulphur. Legumin, prepared by means of salt water from peas and beans, has great resemblance to conglutin from almonds, lupines, &c.

E. W. P.

Ethyl Glycocholate. By A. SPRINGER (*Am. Chem. J.*, **1**, 181—183).—This ethereal salt is prepared by heating crystallised glycocholic acid with hydrochloric acid and alcohol in a sealed tube for about a fortnight, or more readily by passing dry hydrogen chloride through an alcoholic solution of glycocholic acid for 24 hours, and heating the solution in a sealed tube with alcoholic and hydrochloric acid, the tube being opened from time to time to allow escape of gas; the etherification is then completed in about two hours. The ethereal salt being much lighter than the other liquids in the tube, is easily taken from the top. It must be washed with hydrochloric and sulphuric acid, as it is decomposed by water.

Ethyl glycocholate, $\text{C}_{26}\text{H}_{43}\text{EtNO}_5$, thus prepared, is a dark-brown liquid of sp. gr. 0.901. It is decomposed by distillation, also by exposure to the air, leaving a white mass, but may be kept for any length of time in a closed vessel, and heated in a sealed tube to a high temperature without alteration. In contact with water, it forms a

thick brown mass, like dyslysin, which, however, gradually whitens, and deposits crystals of glycocholic acid.

The author has also prepared the ethylic ethers of choloidic acid from ox-bile, and those of hyoglycocholic and hyotaurocholic acids from pig's-bile.

H. W.

Physiological Chemistry.

Influence of the Continued Use of Sodium Carbonate on the Composition of the Blood. By D. DUBELIR (*Monatsh. Chem.*, 2, 295—308).—The author, after citing the results, by no means accordant, deduced by various authors from their observations with reference to this question, gives the results of his own analyses of blood taken from the carotid arteries of dogs, some of which had received definite quantities of sodium carbonate with their food, while others had been kept for equal numbers of days on the same food unmixed with sodium carbonate. From the comparison of these analyses, he deduces the following conclusions:—

1. The continued use of considerable doses of sodium carbonate is attended with a small but perceptible augmentation of the alkalinity of the blood-ash, which increases in strength with the daily quantity of soda added, and the time during which this addition is continued.

2. Potash in the blood-ash is not replaced by soda.

3. Soda does not accumulate in the blood.

4. The proportion of iron, as formerly observed by Nassi, is not diminished by the use of sodium carbonate.

5. The proportion of solid constituents and of nitrogen (albumin) in the blood is not altered by the internal use of sodium carbonate to such a degree as to overstep the normal limits; these, however, have been found to be very variable, *e.g.*, 17·6 per cent. according to Collard de Martigny; 22·2 per cent. according to Forster.

H. W.

The Abnormal Presence of Uric Acid in the Saliva, Gastric Juice, Nasal and Pharyngeal Secretions, the Sweat, Uterine Secretions, and Menstrual Blood. By M. BOUCHERON (*Compt. rend.*, 93, 391—394).—The author remarks that the accumulation in the blood of products which should normally be excreted, leads to toxic effects which are more enduring than those of ordinary poisons, inasmuch as the disordered economy produces them indefinitely. One of the commonest causes of this self-poisoning is uric acid, and the commonest manifestation of it, articular gout. There are, however, a number of other maladies in which the author has been able to detect uric acid in the secretions, and especially in the saliva, which he classes under the following heads:—

- (1.) Uricemia, induced by arrest of the urinary functions or retention of the major part of the materials of the urine.

- (2.) Uricemia induced by a too highly nitrogenised diet.

- (3.) Uricemia of acute gout.

- (4.) Uricemia of chronic articular gout.
- (5.) Uricemia following morbid conditions of the liver, stomach, and intestines.
- (6.) Various lesions of the skin.
- (7.) Of the eye.
- (8.) The ear.
- (9.) Kidney, bladder, and prostate.
- (10.) Following morbid states of the circulatory organs.
- (11.) Lesions of the central nervous system.

The mercurial test was used with ammonia, and found to answer perfectly in all cases. The author is of opinion that examination of the saliva for uric acid will prove useful in the diagnosis of cases of uricemia, and as a guide to the treatment of such cases, both by diet and by the administration of drugs.

W. N.

Diabetic Urine. By A. DEICHMÜLLER (*Annalen*, 209, 22—30). It has been noticed that urine from patients suffering from the more intense forms of diabetes, gives a violet reaction with ferric chloride; and by the distillation of these urines alcohol and acetone are obtained. These phenomena are generally attributed to the presence of ethyl acetoacetate, which would yield equal numbers of molecules of acetone (52) and alcohol (46). Owing to the greater volatility of the acetone, the proportion of alcohol might even exceed that of the acetone; but in all cases hitherto examined the reverse has always been most marked (cf. Abstr., 1879, 560). The author has examined the urine of a youth of 16, suffering from diabetes, which was afterwards complicated with typhus—resulting in death. The urine was acidified and distilled until the distillate gave no reaction with iodine and potassium hydroxide. Potassium carbonate separated from it an oily layer which, after suitable purification, boiled at 56°, and gave the characteristic reactions of acetone. But no alcohol was obtained from 40 litres, even when the patient was taking daily 100 grams of wine containing 15 per cent. alcohol. The author made a series of determinations of the amount of acetone in the urine by mixing the distillate with soda and a solution of iodine in potassium iodide in the cold, and filtering off and finally weighing the iodoform obtained. The exactness of the determination depends on the fact that alcohol in dilute solutions gives hardly a trace of iodoform, whilst acetone is converted into it at once. The percentage of acetone in the urine varied from .093 to .147. Inasmuch as the violet reaction with ferric chloride points to the presence of a compound allied to ethyl acetoacetate, and no alcohol was separable from the distillates, it appears that the compound in question is not *ethyl acetoacetate*, but free *acetoacetic acid*.

V. H. V.

Diabetic Urine. By B. TOLLENS (*Annalen*, 209, 30—38).—The author has examined the question whether the compound in urine, which gives the violet colour with ferric chloride, can be extracted by ether (cf. preceding Abstract). The patient was a labourer 36 years old. On shaking up the urine, which was strongly acid, with ether, only a very slight trace of the ferric chloride reaction was observable

in the extract. But on acidifying the residue with sulphuric acid and repeating the process, the reaction in the ethereal extract was most marked. On slowly distilling another portion of the urine in presence of hydrochloric acid, the distillates gave the iodoform reactions, whilst the residue, even to the end of the distillation, showed the ferric chloride coloration. Similar results were obtained in the case of a woman of 60, suffering from diabetes and mortification of the thigh: and it was further observed that on distillation of the urine, the first few drops which passed over gave a very slight coloration with ferric chloride, but a well-marked iodoform reaction. From these results, the author arrives at the conclusion, that the substance present in the urine is not ethyl acetoacetate, which would, as a neutral body, be taken up by the ether from the non-acidified urine, but the substance must be of an acid nature, and is probably free *acetoacetic acid*. For comparison, the author shows that ethyl acetoacetate can be extracted by ether from neutral or acid, but not from alkaline aqueous solutions. Again from normal, neutral, or acidified urine to which one-tenth of its volume of a 1.5 per cent. of an aqueous ethyl acetoacetate solution was added, the ethereal salt could be extracted by the ether; and the same result was obtained even when the urine was rendered alkaline by the addition of hydrodisodic phosphate. Ethyl acetoacetate may be partially separated from such a mixture with urine as that described above, not only by shaking up ether, but also by distillation.

V. H. V.

Milk of Tyrolese Cows. By K. PORTELE (*Landw. Versuchs.-Stat.*, 27, 133—143).—Several analyses of the milk of three different breeds of cows, under varying conditions, were made according to well-known methods, and the results given in three tables. From these we gather that the evening milk was always richer in solids than the morning milk, and that but little difference was caused in the composition of the milk by change of fodder. No difference was observed in the milk of the three sorts as regards their ash, fat, casein, and albumin constituents. The estimation of fat by means of Fessner's lactoscope proved untrustworthy, whilst the polarimetric determinations of lactose agreed very well with the numbers obtained by the use of Fehling's solution. The percentage amounts of milk constituents varied between the following limits:—Fat, 3.06—4.82; solids, 11.13—13.85; nitrogen, 0.433—0.579; nitrogenous substances, 2.71—3.62; casein, 2.16—3.00; albumin, 0.31—0.59; milk-sugar, 4.28—5.37; and ash, 0.539 to 0.77 per cent.

J. K. C.

Chemistry of Vegetable Physiology and Agriculture.

Bark of *Sambucus Canadensis*. By C. G. TRAUB (*Pharm. J. Trans.* [3], 12, 186).—The air-dried drug contained 13 per cent. water and 8·5 per cent. ash. It contained valeric acid, volatile oil, fat (soluble in ether and chloroform, and saponifiable by potash), resin,

tannin, sugar, and colouring matter, together with several other compounds, the nature of which was not determined. C. H. B.

Analysis of Buckwheat. By G. LECHARTIER (*Compt. rend.*, **93**, 409—412).—On account of the discordant analyses of buckwheat, the author has analysed the straw and grain of samples of buckwheat in the years 1879 and 1880, taken from the commune of Cisson.

The ratio of the weight of straw to grain was 0·920 in 1879, and 1·585 in 1880.

Ashes of Buckwheat.

	Straw.		Grain.	
	1879.	1880.	1879.	1880.
Potash	22·57	44·01	28·40	25·73
Soda	2·12	1·71	4·17	0·77
Lime	34·94	21·66	6·33	10·17
Magnesia	16·22	7·49	18·10	15·06
Oxide of iron	1·79	1·66	0·73	0·30
Phosphoric acid	3·32	8·29	38·05	43·47
Silica	4·82	0·61	traces	0·29
Sulphuric acid	3·76	2·51	3·54	3·93
Chlorine	10·44	12·06	0·67	0·63

Of these analyses the author observes that the differences between the composition of the straw and grain are similar to those in wheat. On comparing the results of the two years, it is found that the ashes of the straw contained more potash, phosphoric acid, and chlorine in 1880 than in 1879; the ashes of the grain present slighter differences. In 1879 the weight of the straw was less than the grain, whilst the reverse was the case in 1880. These facts are in accordance with the method of vegetation of buckwheat, which differs considerably from other cereals, for the panicles of the flower grow at the axis of the leaves before the plant has reached its mean height; it continues to throw out branches covered with flowers while the grain is ripening.

Analysis (parts per 1,000) of Straw and Grain.

	Dried Straw.		Dried Grain.	
	1879.	1880.	1879.	1880.
Ash	62·34	77·43	18·55	23·50
Nitrogen	8·90	12·29	19·13	23·17
Potash	14·08	33·95	5·06	6·15
Soda	1·32	1·32	0·78	0·18
Lime	22·37	16·99	1·12	2·39
Magnesia	10·11	5·78	3·22	3·54
Oxide of iron	1·11	1·28	0·12	0·07
Phosphoric acid	2·07	6·39	6·79	10·22
Silica	3·01	0·47	nil	0·07
Sulphuric acid	2·35	1·94	0·63	0·92
Chlorine	6·40	9·32	0·12	0·15

The composition of the grain varies but little, but the quantities of mineral constituents of the straw, especially phosphoric acid, chlorine, and potash, increase relatively with its weight. The quantities of fertilising principles abstracted from the soil is very considerable, even greater than in the case of wheat for the same weight of grain.

V. H. V.

Analyses of Fodder. By G. FASSBENDER (*Landw. Versuchs.-Stat.*, 27, 123—131).—The albumin was determined by Stutzer's method of precipitation with cupric hydroxide; this reagent is most conveniently kept in glycerol when not required. The amount of digestible nitrogen was estimated by exhausting with a liquid obtained by soaking pig's stomach in dilute hydrochloric acid. The results are given in the following table:—

	Total N p. c.	In per cent. of total N.		
		Not precipitated by CuH_2O_2 .	Precipitated by CuH_2O_2 .	
			Digestible.	Indigestible.
Rye bread	1·915	10·18	75·62	14·20
White do.	1·67	2·51	93·18	4·31
Egg albumin.	—	—	—	—
Blood meal	7·037	1·18	83·48	15·34
Cocoa-nut cake. . .	2·585	—	78·34	21·66
Ground-nut do. . .	8·505	4·53	92·40	3·07
Lupines.	6·76	14·13	83·83	2·04
Malt combings . .	2·856	21·92	61·65	16·56
Meadow hay	1·605	21·67	43·66	34·67
Swedes	2·57	63·42	26·00	10·58

J. K. C.

Absorption of Salts by the Soil. By C. F. A. TUXEN (*Landw. Versuchs.-Stat.*, 27, 107—113).—The object of this investigation was to ascertain what influence sodium nitrate and chloride and potassium chloride have on the absorption by the soil of potash, ammonia, and phosphoric acid. Two kinds of soil were employed, one sandy and containing 92·5 per cent. of silica and 6·8 per cent. of bases, and the other of a clayey nature, and containing 82·1 per cent. silica and 15·8 per cent. bases. For each experiment 100 grams of the sifted and dried earth were mixed with 100 grams fine sand, and the whole shaken into a glass tube fitted at the lower end with a stopcock. The height of the mixture in the tube was 22 cm. A salt solution of a given strength, containing an ammonium or potassium salt or a phosphate, was then allowed to trickle slowly through the earth for 48 hours. Some of the solutions were mixed with sodium nitrate or chloride, or potassium chloride, in order to ascertain their influence on the absorption of the other salts. The amount of ammonia, potash, or phosphoric acid, was estimated in the first 100 c.c. of the solution which passed through. The original solutions were of the following strengths:—ammonia, 100 c.c. nitrogen at 0°, and 760 mm. in 100 c.c. solution; potash, 0·47 gram in 100 c.c.; phosphoric acid, 100 c.c. contained 0·355 gram. The quantities of other salts mixed with 100 c.c. of these solutions were sodium nitrate, 0·850

gram; sodium chloride, 0·585 gram; and potassium chloride, 0·745 gram. The following table shows the percentages of ammonia, potash, and phosphoric acid absorbed:—

Solution.	Ammonia absorbed.	
	Sand.	Clay.
Ammonia alone.....	27·2	89·0
„ with sodium nitrate	24·6	84·5
„ „ „ chloride....	25·9	83·0
„ „ potassium chloride .	16·4	57·0

	Potash absorbed.	
	Sand.	Clay.
Potash alone.....	23·4	83·2
„ with sodium nitrate	20·0	67·2
„ „ „ chloride	19·1	7·44

	Phosphoric acid absorbed.	
	Sand.	Clay.
Phosphate alone	26·8	71·6
„ with sodium nitrate	30·8	80·0
„ „ „ chloride ..	30·8	80·0
„ „ potassium chloride	35·2	86·0

From the above table it will be seen that there is a great difference in the absorptive powers of the two soils, also that the absorptive power for ammonia is lessened by potash; in sand to the extent of 40 per cent., and in clay by 36 per cent., and by soda only 8 and 6 per cent. respectively. Soda lowers the absorption of potash also 15 per cent. in each soil. On the other hand, phosphoric acid is more readily taken up in the presence of alkalis, more especially of potassium salts. The mixing of phosphate manures with potassium salts is therefore to be recommended.

The question next arose as to whether solutions of sodium nitrate or chloride had a greater solvent power on the combined potassium and phosphate in soil than pure water. 100 grams of the clay soil were shaken for two days with 200 c.c. of the liquids in question. The quantities of substances dissolved may be seen from the table annexed:—

	Water.	Sol. NaNO_3 .	Sol. NaCl .
Lime.....	0·019	0·094	0·109
Magnesia	0·003	0·008	0·022
Potash	0·001	0·005	0·007
Phosphoric acid ..	0·002	0·006	0·003

Solutions of sodium salts have therefore a much greater solvent power than pure water. J. K. C.

Grandeau's Theory of the Fertility of a Soil. By C. F. A. TUXEN (*Landw. Versuchs-Stat.*, 27, 114—121).—An attempt was made to ascertain the worth of this theory by its application to soils of

known fertility. Soils 1, 2 and 3 came from a field near Copenhagen, and contained 26·5 per cent. clay and the rest sand. No. 1 was in a high state of cultivation, having been manured well with dung and artificial manures since 1863: average yield of last 5 years, twenty times the seed. No. 2 had received no manure for 21 years, and for the last 17 years had been sown with barley: average produce of last 5 years three times the seed. No. 3 had for 17 years been manured only with artificial manures, and had received no stable dung: average crop of last 5 years nineteen times the seed. No. 4 consisted of decayed leaves mixed with an equal quantity of fertile soil, and contained 10·64 per cent. humus. No. 5 was Nile slime, taken from the neighbourhood of Cairo, and very fertile.

The amount of soil dissolved by hydrochloric acid in setting free the *matière noire* of Grandeau is given below in grams per hundred of the sample:—

	No. 1.	No. 2.	No. 5.
Ferric oxide }	0·438	0·170	4·192
Alumina }			
Lime	0·532	0·110	1·653
Magnesia	0·005	0·007	—
Potash	0·010	0·003	0·091
Phosphoric acid ..	0·058	0·013	0·200
	1·043	0·303	6·136

The dilute acid therefore dissolves a large quantity of the nutritive material. Determinations of the *matière noire*, and the organic matter, ash, and phosphoric acid contained therein, were then made in the different soils, in order to test the value of Grandeau's theory as an indicator of fertility. The mean results are given in the table below in grams per 100 of earth.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Matiere noire	1·68	1·62	1·55	2·23	2·64
Loss on ignition ..	1·33	1·07	1·07	1·85	1·23
Ash	0·35	0·55	0·48	0·38	1·41
Phosphoric acid ..	0·098	0·076	0·09	0·12	0·085

The difference in fertility between the soils 1 and 2 cannot therefore be ascertained by simply estimating the amount of *matière noire*, nor does this give any indication of the relative value of the other soils. Experiments were made to find if there was any difference in the diffusive power through vegetable membranes in the different kinds of black substance, but none was observed. In the case of these five sorts of soil therefore, the results given by the use of Grandeau's method did not agree with those obtained by practical experience.

J. K. C.

Manuring Experiments with various Phosphates. By KROCKER and H. GRAHL (*Landw. Versuchs-Stat.*, 27, 151—160).—The phosphates used were in the form of retrograde, precipitated, and soluble phosphoric acid, and bone-meal. They were employed in quantities in the proportion of 50 kilos. phosphoric acid per hectare.

The land consisted of a heavy clay soil, well drained, and was sown with oats, beetroot, and potatoes; the phosphates were applied both by themselves and mixed with ammonium sulphate to the extent of 200 kilos. per hectare, and one plot was left unmanured: good crops of oats were produced, but no increase of yield was obtained by the use of phosphates alone, except in the case of bone-meal, which contained 4 per cent. of nitrogen. Where ammonium sulphate was mixed with the manure, a considerable increase was observed, especially in the case of the precipitated phosphate and bone-meal. Similar differences were observed in the beet, but not to so large an extent, and here the soluble phosphate produced larger yields than the other kinds when given by itself, or in conjunction with ammonium sulphate, although it proved inferior to bone-meal in the first case. The highest percentages of sugar were obtained from the plots manured with sulphate alone and with retrograde phosphate, and from the unmanured plot.

J. K. C.

Analytical Chemistry.

A Solution of Density 3.28 suitable for the Analysis of Minerals. By M. D. KLEIN (*Compt. rend.*, **93**, 318—320).—Inasmuch as the density of most minerals ranges from 2.2 to 3.3, they can be easily separated from one another by immersion in solutions without chemical action on them. Solutions of mercuric iodide in potassium iodide have partly fulfilled the necessary conditions, but the minute precautions required have prevented the general introduction of this method. Nearly saturated solutions of the cobalt, nickel, and cadmium borotungstates prepared by the author have sp. gr. about 3.28—3.31. The dark tint of the two former salts renders their solution comparatively useless for the purpose, but the cadmium salt solution being of a very pale yellow colour is very suitable. The author illustrates how, for instance, by this solution a diamond can be distinguished immediately from white sapphire or colourless corundum. In order to prepare this solution, tetrasodic borotungstate (this vol., 224) is converted into barium borodecitungstate (*Abstr.*, 1880, 612), and then decomposed by cadmium sulphate. The solution is evaporated on a salt-water bath until a fragment of peridot swims on the surface; then on cooling orthorhombic crystals of the cadmium salt are deposited. The crystals melt at 75° in their water of crystallisation and retain their mother-liquor, and there is formed a mobile liquid of the required density, 3.6. V. H. V.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. By F. A. GOOCH (*Am. Chem. J.*, **1**, 391—413).—This paper gives the results of a large number of analyses of alkaline phosphates, phosphotungstates, and phosphomolybdates, from which the following conclusions are drawn:—

In determining the phosphoric oxide of *alkaline phosphates* free from sulphates or other substances likely to contaminate a precipitate, accuracy is most conveniently and surely attained by adding to the somewhat dilute solution of the phosphate, first ammonia in slight but distinct excess, then an excess of magnesium chloride mixture containing free ammonia (made by dissolving 3 parts crystallised magnesium chloride and 8 parts ammonium chloride in water, adding water containing ammonia till the volume of the solution amounts to 48 parts, then filtering and boiling off the free ammonia), and after the precipitate has settled, adding a further excess of ammonia till the liquid smells strongly of it.

In determining the phosphoric oxide of *phosphotungstates*, the best results are obtained by adding to the solution containing free ammonia, an excess of either of the magnesia mixtures, washing the precipitate with the precipitant, dissolving in hydrochloric acid, diluting if necessary, and reprecipitating with a little dilute ammonia, adding strong ammonia after the precipitate has settled; or, when working with small amounts, by proceeding as in the case of the phosphates, taking however special care that the solution is distinctly ammoniacal before precipitating, and that no great excess of the precipitant is used. For the determination of phosphoric oxide in *phosphomolybdates*, the method recommended in the case of the phosphates serves very well when the amount of phosphoric oxide does not exceed about 0.05 gram, but for larger amounts, the method of double precipitation recommended for the phosphotungstates is more accurate.

With regard to the time which should be allowed to pass between precipitating and filtering, the author's experiments support those of Abesser, Jani, and Maercker (this Journal, 1874, 387) in pointing to the condition that a precipitate may safely be filtered as soon as it has completely subsided, generally after ten or fifteen minutes.

H. W.

Estimation of Potassium as Platinochloride. By D. LINDO (*Chem. News*, **44**, 77, 86, 97, 129).—A moderate excess of platinum chloride solution, containing about 1 gram of platinum in 20 c.c., is added to the somewhat dilute solution of alkaline chlorides, the liquid evaporated to dryness on the water-bath, and then heated for two or three minutes. The residue is washed three or four times with alcohol of 98 per cent., then carefully crushed with a glass rod, and again washed repeatedly with alcohol, Gooch's method of filtration (*Chem. News*, **37**, 181) being employed. The platinochloride was dried at 130°. The results obtained were very accurate, even in presence of 50 per cent. sodium chloride. The double salt is not hygroscopic, and there is no need to place the crucible in a desiccator whilst cooling. When using Tatlock's method, the author finds that the platinum tetrachloride solution employed for the first washing dissolves a small quantity of the double salt, and consequently the results obtained are somewhat too low. Even in presence of excess of platinum chloride, it would appear that sodium chloride is not entirely converted into the double salt or, more probably, that reversion takes place either during evaporation or on adding the alcohol. Prolonged heating of the residue on the water-bath promotes rever-

sion, which may be prevented by employing a moderate excess of platinum chloride, and taking care not to heat the platinochlorides too long after they have become dry. Direct experiments showed that potassium platinochloride is practically insoluble in absolute or very strong alcohol; when the platinochloride is in the form of scales, alcohol of 80 per cent. dissolves a small quantity; when in the form of powder, alcohol of 80 per cent. dissolves a quantity sufficient to sensibly affect the results. The author finds that potassium platinochloride is very slightly soluble in a half saturated solution of ammonium chloride, and proposes to use a solution of the latter to wash out any magnesium and sodium sulphates, &c., with which the platinochloride may be mixed. The double salt is first thoroughly washed with alcohol, then with an aqueous solution of ammonium chloride, and finally with alcohol. If accurate results are desired, the ammonium chloride solution should be saturated with platinochloride before being used. Taking the atomic weight of platinum as 197.18, the mean of the determinations of potassium chloride was 100 per cent.; taking Seubert's number 194.46, the mean was 100.55 per cent.

C. H. B.

Electrolytic Estimation of Zinc. By H. REINHARDT and R. IHLE (*J. pr. Chem.* [2], **24**, 193—201).—It is found that the usual processes for the electrolytic estimation of zinc are all to a certain extent unsatisfactory. The presence of free sulphuric acid and ammonium acetate are especially prejudicial to the results. The following modification is therefore proposed: the anode consists of a spiral of strong platinum wire, and the cathode of a cone of platinum suspended above the anode, the distance between the two being 5 mm., and the surface of the latter 160 sq. cm. The object of the peculiar form of cathode is to ascertain, by lowering it into the liquid, if the last trace of metal has been removed. The negative electrode is to be previously coppered, and nitric acid may be employed for removal of the deposited zinc, as the copper is not attacked in the cold. The copper coating must be even and clear, otherwise the zinc will be deposited in numerous small loosely attached grains. The zinc is deposited from a solution of the oxalate, and for this purpose the neutral chloride or sulphate solution is mixed with an excess of potassium oxalate until the precipitate produced is redissolved; the metal is precipitated from this solution at the negative pole, and may be easily washed with water. This process works well with alloys.

E. W. P.

Reduction of Iron Ores by Powdered Zinc. By T. M. BROWN (*Chem. Centr.*, 1881, 75).—An intimate mixture of 0.3 gram powdered ore with 10 times as much finely pulverised zinc is placed in a porcelain crucible and covered with an equal weight of powdered zinc. The open crucible is heated for ten minutes over a Bunsen burner to dark redness. On cooling, the whole contents of the crucible are rapidly dissolved in hydrochloric acid out of contact with air, and the iron is determined by potassium permanganate in the usual manner. Bituminous ores must be roasted before reduction. To prevent the introduction of organic matter from the lamp, a layer of borax is

placed above the layer of zinc. Powdered zinc is also found to have advantages over granulated zinc and sheet zinc in the reduction of ferric to ferrous solutions.

F. L. T.

Separation of Cobalt and Nickel from Iron. By T. MOORE (*Chem. News*, **44**, 76).—The solution, which should not contain much free acid, is mixed with ammonium sulphate in quantity sufficient to form a double sulphate with the cobalt and nickel present. The solution is then diluted to about 150 c.c., mixed with a large excess of oxalic acid and well stirred. If a precipitate is formed, it must be redissolved by further addition of ammonium sulphate. The clear liquid is mixed with ammonia in slight excess, heated gently for a few minutes, filtered, and washed with water containing ammonia, or the liquid is diluted to a known volume and, after the precipitate has settled, a definite quantity of the clear liquid is drawn off and the nickel determined by electrolysis or otherwise.

C. H. B.

Separation of Tungsten from Antimony, Arsenic, and Iron, together with the Analysis of a so-called Pseudometeorite. By A. COBENZL (*Monatsh. Chem.*, 1881, 259—265).—The metallic mass which is the subject of this examination, was found in 1879 at Cista in Bohemia. Externally it exhibits some of the characters of meteoric iron, but as its fall was not actually observed, and as its physical and chemical characters were found on closer examination to differ from those of well authenticated iron meteorites, it has been designated a pseudometeorite. It is brittle, easily pulverisable, and has a fine-grained confusedly crystalline texture, revealed by the shimmering aspect of its newly fractured surface, whereas meteoric irons are tough and have a hackly fracture. Moreover, the pseudometeorite is porous and has a blistered surface, the character of which is more like that of certain furnace-products than that of meteoric iron. The colour of this metal is violet-grey, differing therefore from the neutral grey of meteoric iron.

Qualitative analysis showed that the chief constituents of the pseudometeorite are iron, tungsten, antimony, and arsenic, associated with small quantities of water and insoluble silicates (ferric oxide, alumina, lime, magnesia), carbon, and sulphur; traces of bismuth and tin were also detected.

The quantitative analysis presented peculiar difficulties in the separation of the first four constituents above mentioned, respecting which no exact statements are to be found in chemical literature. The following method was found by the author to yield satisfactory results. The mineral, very finely pulverised and sifted through linen, was drenched in a flask with strong nitric acid, and heated on a water-bath for four or five days, with occasional addition of hydrochloric acid, till nothing was left undissolved but pure yellow tungstic acid. The solution, together with the tungstic acid, was evaporated to dryness over a water-bath; the dry dusty residue redissolved in very dilute nitric acid; the solution again evaporated to dryness, and this treatment three times repeated. The residue was then dissolved in very dilute nitric acid, with addition of a small quantity of tartaric

acid, the solution evaporated at 100° and filtered, and the separated tungstic acid several times washed by decantation with boiling acidulated water, and finally collected on a filter.

The solid matter thus separated contained the whole of the tungsten, together with silica, and silicates undecomposable by acids, whilst all the other metals, together with lime and alumina, were found in the filtrate. The tungstic acid was treated on the filter with very dilute ammonia, which dissolved it, leaving behind the silica and silicates. The ammoniacal solution was evaporated to dryness in a weighed porcelain crucible, the residue ignited, and the pure straw-yellow tungstic acid thus obtained was weighed. The undissolved silicates were dried, ignited, weighed, and analysed in the usual way by decomposition with a mixture of potassium and sodium carbonate. The filtrate from the tungstic acid was saturated with yellow ammonium sulphide, whereby iron sulphide and alumina were precipitated, while arsenic, antimony, and lime remained dissolved. All these constituents were separated and estimated by the usual methods.

The sulphur, after separation of the tungsten, was weighed as barium sulphate. The carbon was estimated, together with the water, by igniting the powder in a stream of oxygen, and collecting the water and carbonic acid in the usual way. The amount of oxygen was determined by reducing the oxides present in a stream of hydrogen. The results of the analysis were as follows:—

Fe.	W.	Sb.	As.	Silicates.	H ₂ O.	Al ₂ O ₃ .
56.07	25.39	9.85	5.08	1.55	0.78	0.60
	CaO.	O.	C.	S.		
	0.37	0.28	0.18	0.053		

The percentage composition of the silicates was found to be:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.
41.2	26.8	18.0	14.0

From the physical and chemical characters above described, it may be inferred almost with certainty that this substance is not an actual iron meteorite, but a furnace-product, such as were often obtained in the early days of the metallurgic preparation of tungsten. The following table exhibits a comparison of its chief constituents, and its specific gravity, with those of iron meteorites:—

Mean of iron meteorites.			Pseudometeorite.	
Iron	81 to 98	p. c.	Iron	56.4
Nickel	3	17	Tungsten ..	25.3
Phosphorus..	0	1	Antimony ..	9.9
Cobalt	0	2.6	Arsenic	0.1
Sp. gr.....	6.6	7.9	In the lump .	8.854
			In powder ..	8.8993
			H. W.	

Action of Potassium Permanganate on Potable Waters at Different Temperatures. By G. W. WIGNER and R. H. HARLAND (*Analyst*, 1881, 39).—The experiments of the authors show that the

amount of oxygen absorbed by potable waters when mixed with potassium permanganate varies considerably with the nature of the water and with the time, and in some cases with the temperature. The nature of the pollution also has a marked effect on the oxygen absorbed, but no general conclusions can be drawn from their results.

L. T. O'S.

Estimation of Nitrates in Potable Waters. By J. WEST-KNIGHTS (*Analyst*, 1881, 56—58).—The author applies the brucine test for nitric acid to the estimation of nitrates in potable waters, the blood-red colour being permanent if oxalic acid is used instead of sulphuric acid, in applying the test to nitrates. For the purpose are required a potassium nitrate solution containing 0.721 gram per litre (1 c.c. = 0.0001 gram N as NO_3), a brucine solution (1 gram in 100 alcohol), a cold saturated solution of oxalic acid, and a *standard red solution* prepared by evaporating 10 c.c. of the potassium nitrate solution to dryness, and adding 3 c.c. of the brucine solution and 6 drops of oxalic acid solution, evaporating to dryness, dissolving the residue in water, and again evaporating; the residue is dissolved in residue and made up to 100 c.c. This solution should have a bright-red colour, and 1 c.c. of it is equal to 0.00001 nitrogen as nitrate.

The water to be examined is prepared in a similar manner. 10 c.c. are evaporated to dryness, and from 0.5 to 2 c.c. of brucine solution added to the residue. The brucine should be just in excess, and the colour a bright red; if it be brown, a fresh quantity of water must be taken, and a larger quantity of brucine added; but if the colour is pink, a smaller quantity of brucine must be used. Three or four drops of oxalic acid are added to the residue, which is treated as in the case of the standard solution, except that the residue after the final evaporation is dissolved in a small quantity of water, filtered into a glass cylinder, and the volume made up to 50 c.c., and the colour compared with from 1 to 10 c.c. of the standard colour. If the colour produced by the water is deeper than that of 10 c.c. of the standard, it must be diluted with two or three volumes of water, and 50 c.c. treated as before; but if it be lighter than that of 1 c.c., a larger quantity of water must be used to begin with.

L. T. O'S.

Estimation of Nitrates in River Water. By F. P. PERKINS (*Analyst*, 1881, 58—59).—The author applies a magnesium-platinum couple in presence of sodium chloride to the reduction of nitrates in river water.

L. T. O'S.

Detection of Lead in Potable Waters. By S. HARVEY (*Analyst*, 1881, 146—148).—Potassium dichromate is a more delicate test than sulphuric acid or potassium iodide for the presence of lead in water. It is also preferable to sulphuretted hydrogen, since in the event of copper or tin being present in the water, there is a difficulty in distinguishing between the precipitates. It is possible to detect one-fiftieth of a grain of lead per gallon by this means, even in presence of sulphates. The potassium dichromate is added in the solid state.

L. T. O'S.

Assay of Wood Spirit for the Preparation of Methylated Spirit. By C. BARDY (*J. Pharm.* [5], 4, 129—135).—The author describes a method for the estimation of methyl alcohol in wood spirit, which consists in the comparison of the amount of iodoform obtained from the sample with that from a standard wood spirit. For the purpose, a standard solution of caustic soda is prepared, and a solution of 254 grams iodine and 385 potassium iodide in 1 litre of water.

5 c.c. of the wood spirit to be assayed is diluted to 50 c.c. with water, and 10 c.c. of this solution is made up to 1 litre with water, and 5 c.c. of this is placed in a tube with 10 c.c. soda solution and .5 c.c. of the iodine solution. After well shaking, 30 c.c. of water are added, and the milkiness due to the formation of iodoform is compared with that in a similar solution prepared from the standard wood spirit. The comparison is effected by placing behind the tubes a white card, marked with a number of black lines of various thicknesses, and noting the number of lines visible in each case. The comparison should be made immediately, since the iodoform settles after the lapse of a short time. Should the milkiness be less than that produced by the test solution, the wood spirit is too rich in methyl alcohol, and cannot be used.

If the milkiness is alike in both cases, or greater in the case of the sample than in that of the test, it is necessary to estimate the methyl alcohol by Bardet and Bordet's method.

This method cannot be used if the wood spirit contains a large proportion of aldehyde, which is detected by diluting the wood spirit with 10 of water, and adding to 5 c.c. of the diluted spirit 2 c.c. of aqueous solution of magenta (0.20 grain per litre), decolorised by sodium thiosulphate, when a violet colour is produced, varying in intensity with the quantity of aldehyde present. The aldehyde is estimated by distilling 5 c.c. of the wood spirit, with 7 c.c. of sulphuric acid, diluted with 10 c.c. of water. The value of the spirit may then be estimated as above.

In assaying wood spirit, it is necessary that it should contain no ethyl alcohol, accidentally or fraudulently added, and no methyl ethers. The latter are estimated by saponification. The estimation of alcohol, mixed with wood spirit, is effected by diluting 10 c.c. to 1 litre with water, and proceeding as above.

If essences are present, 11 c.c. are diluted, and the solution filtered through a moist filter-paper. To estimate varnishes prepared with methylated spirit, 11 c.c. are distilled to dryness, the distillate diluted to a litre, and the above method applied.

L. T. O'S.

Volumetric Estimation of Glycerol. By J. MUTER (*Analyst*, 1881, 41—46).—The power of glycerol to prevent the precipitation of copper by potash from its solutions is made use of for the estimation of glycerol. 1 gram glycerol is washed into a stopper-graduated tube with a stopcock 50 c.c. from the bottom (Muter olein tube), and 50 c.c. of potassium hydroxide (1—2) added. A dilute copper sulphate solution is then carefully run in, with constant shaking, until a fair amount of copper hydroxide remains undissolved ;

the whole made up to a given volume and allowed to settle. When clear, a given volume is made slightly acid with nitric acid, a definite excess of ammonia added, and finally titrated with potassium cyanide solution, of which 1 c.c. = 1 gram glycerol. By using pure potassium cyanide made from the acid, good results may be obtained; there is a slight deficiency, however, owing to the difficulty of working the cyanide estimation of copper to a constant point. In cases where the amount of glycerol to be estimated is very small, the copper is determined by electrolysis on platinum.

L. T. O'S.

Detection of Hydrocyanic Acid. By E. LUDWIG and J. MAUSHNER (*Chem. Centr.*, 1881, 43—44).—In a poisoning case submitted to the authors, potassium ferrocyanide was shown to be present, and was removed by slightly acidulating and carefully precipitating by ferric chloride. On submitting the filtrate to distillation with tartaric acid, a distillate was obtained both from the contents of the stomach and from the residue in the bottle containing much hydrocyanic acid.

The sample of potassium cyanide which is supposed was employed was subsequently found to contain a very considerable quantity of ferrocyanide.

F. L. T.

New Demonstration of Carbonic Anhydride in the Breath. By C. F. CROSS (*Chem. News*, 44, 141).—When respired air is blown into a solution containing a mixture of potassium iodide and iodate and starch, the carbonic acid causes the liberation of iodine, and consequent production of a blue coloration. Direct experiments proved that the liberation of iodine is not due to the action of the oxygen of the air, or to the accidental presence of acid vapours.

C. H. B.

Determination of Salicylic Acid in Food-stuffs by a Colorimetric Reaction. By H. PELLET and J. DE GROBERT (*Compt. rend.*, 93, 278—280).—The method of determining salicylic acid by the titration of the residue obtained by an ethereal extract gives too high results, from the solubility of other acids in the ether. On the other hand, on substituting benzene for ether too low results are obtained from the volatilisation of salicylic acid during evaporation. The author has modified the colorimetric method proposed by Rémont: a set of eight assay-tubes are prepared containing quantities varying from 1 c.c. to 0.05 c.c. of solution of salicylic acid (1:1000), and the volume filled up with water to 10 c.c.; to these are added 3 to 1 drops of a dilute solution of ferric chloride (sp. gr. 1.005—1.010). In order to estimate the quantity of salicylic acid in wine, for example, 100 c.c. of it are shaken up with 100 c.c. ether and a few drops of sulphuric acid; the supernatant ether is drawn off and rapidly distilled. A quantity of soda solution is then added, more than capable of saturating the salicylic acid likely to be present, and the whole is evaporated to dryness on a water-bath to drive off the excess of acetic acid extracted by the ether. The residue obtained is rendered acid by sulphuric acid, 20 c.c. of benzene added, and the solution filtered; 10 c.c. of the solution is then dropped into an assay-tube, mixed with 10 c.c. water,

and 1 to 2 drops of ferric chloride added; the mixture is shaken up, and the tint compared with one of the standard assay-tubes. The author adduces experiments in support of the accuracy of this method.

V. H. V.

Estimation of Tannin in Tea. By A. HILL (*Analyst*, 1881, 95—99).—The author uses Löwenthal's method (*Zeits. Anal. Chem.*, 1877, 3, and 201) for the estimation of tannin in tea, and from the analysis of thirty-two samples of black and green tea, it would seem that, as a rule, green tea is richer in tannin than black. The total average amount is 14.8 per cent. The author's results, although obtained from the undried leaves, agree on the whole with those of Mulder, who worked with dried leaves.

L. T. O'S.

Estimation of Quinine. By A. W. BLYTH (*Analyst*, 1881, 162—164).—The volumetric estimation of quinine is effected by a standard solution of Mayer's reagent containing 13.456 grams mercuric chloride and 49.8 grams potassium iodide per litre. The complete precipitation is determined by testing a drop of the clear solution. The drop is extracted by means of a "filter-tube" consisting of a glass tube, widened at one end into a funnel shape; the widened end is packed with glass wool, and the tube used as a pipette. To estimate quinine in wine, it is first precipitated with Scheibler's reagent, and the precipitate shaken with strong soda solution and ether in a tube of special construction, which cannot be described without the aid of a diagram.

L. T. O'S.

Isolation of Strychnine. By A. H. ALLEN (*Analyst*, 1881, 141—142).—The author advocates the use of a mixture of ether and chloroform in equal volumes for the separation of recently precipitated strychnine from its aqueous solution. This solvent is preferable to ether or chloroform alone, since the former has not sufficient solvent power, and the latter does not separate readily from the aqueous solution.

L. T. O'S.

Analyses of Milk. By B. DYER (*Analyst*, 1881, 59—62).—The analyses of the milk of cows, stall-fed and at grass, show that that of the former is the richer, and that an individual cow well fed can frequently give milk yielding an average of 8.7 per cent. solids, not fat. It is therefore necessary to take into account the percentage of fat as well as that of "solids not fat" before pronouncing on cases of adulteration.

L. T. O'S.

Analyses of Milk. By C. A. CAMERON (*Analyst*, 1881, 75—78).—The analysis of the milk of forty-two cows kept at the Government Agricultural Institution, Glasnevin, shows—

(a.) That the quantity and quality of the milk improves as the age of the cow advances.

(b.) That towards the end of the period of lactation, although the quantity of milk becomes less it improves, on the whole, in quality.

(c.) That the milk given in the evening is as a rule richer than that given in the morning.

The results of the analysis of the mixed milk from eight of the forty-two cows when it is poorest, *i.e.*, in the morning, are as follow :—

Total solids	13.90 per cent.
Solids not fats	9.75 „
Fats.....	4.15 „
Ash.....	0.72 „

The author bears out the statement of Dyer (preceding Abstract), that the standard of solids not fat is too high, and proposes that 8.5 should be taken as a minimum; but in no case should the total solids be less than 11.5. The minimum for fats he considers too low, and would raise it to 2.75.

The author also advocates the use of a second general standard : solids not fats, 9 per cent.; fats, 3 per cent. L. T. O'S.

Action of Organic Matter, not Sugar, in Cane and Beet Products on Alkaline Copper Oxide Solution. By J. H. TUCKER (*Chem. News*, 44, 29).—It has been stated that the organic substances in commercial sugars and syrups have a reducing effect on Fehling's solution, and therefore it is recommended to remove them by means of lead acetate before determining the amount of sugar. The author finds that such organic matters exert so little influence on the result of the analysis, that their removal is not necessary, unless they are present in considerable quantity. C. H. B.

Estimation of Gluten in Flour. By BÉNARD and J. GIRARDIN (*J. Pharm.* [5], 4, 127—128).—In estimating the gluten in flour by the ordinary method, it is necessary to allow the paste to stand for at least three hours before washing out the starch, otherwise a considerable loss of gluten (5—6 per cent.) occurs; and in all cases where two determinations in one sample are made, should the same conditions of time be observed.

It is preferable to estimate the gluten after drying it at 110—120°. L. T. O'S.

Method for Examination of Coffee. (By F. M. RIMMINGTON (*Analyst*, 1881, 2).—The presence of chicory, dandelion, &c., in coffee, may be ascertained by boiling with sodium carbonate, and then heating with dilute bleaching-powder solution, when the chicory and dandelion are bleached, the coffee being unacted on. L. T. O'S.

Separation of Wool and Silk in Textile Fabrics. By A. RÉMONT (*J. Pharm.* [5], 4, 135—138).—To determine the nature of the fabric, a portion is boiled with hydrochloric acid (5 per cent.), washed and dried, the warp and weft are separated and burnt separately. If an odour of burnt horn is evolved, and ammonia is evolved when boiled with sodium hydroxide, it is plunged into boiling basic zinc chloride.

A. Solution is complete—silk.

B. On addition of hydrochloric acid, copious flocculent precipitate—silk mixed with wool or vegetable fibres.

C. Insoluble in zinc chloride, but on boiling with caustic soda. Completely soluble—wool.

Partially soluble—wool and cotton.

It does not evolve an odour of burnt horn—vegetable fibres.

Quantitative estimation, four pieces of the cloth of 2 grams are taken.

Estimation of Size and Dye.—Three of the pieces are boiled with 200 c.c. hydrochloric acid (3 per cent.) for a quarter of an hour, the solution decanted, the operation repeated, the fragments washed with water and dried. The size is thus removed, and also the colouring matter, if the material is cotton, but in the case of wool and silk the latter is only imperfectly removed.

Silk, however, dyed with aniline colours contains such a small quantity of colouring matter that it may be neglected; but silk dyed black with logwood and iron can be charged indefinitely with colouring matter, and then the colouring matter may be roughly estimated by ignition and weighing the ferric oxide. Should the proportion of ferric oxide amount to 5, 8, or 10 per cent., it is necessary to take account of it.

Separation of Silk.—Two of the fragments are plunged for two minutes in a boiling solution of basic zinc chloride (1.69 sp. gr.), then thrown into water, and washed in acid water, and finally in water until the wash-water gives no precipitate with ammonium sulphide.

Separation of Wool.—One of the pieces, after treatment with zinc chloride, is dried, and boiled gently with 60—80 c.c. soda solution (1.02 sp. gr.) for a quarter of an hour, care being taken not to destroy the vegetable fibres.

The four pieces of cloth are then dried for an hour at 100° and then left until the next day in the same atmosphere as the original specimen is kept, when they are weighed. The piece of cloth which has not been treated should weigh 2 grams; but all differences above 5 mgrms. must be taken account of in estimating the proportions of size and colouring matter, silk, wool, and vegetable matter, which are obtained by difference from the various weights.

L. T. O'S.

Technical Chemistry.

Coloured Photographs. By J. ALBERT (*Chem. Centr.*, 1881, 78).
—The author takes three negatives of the object, taking care to exclude yellow, blue, and red rays in the three cases respectively. The negatives are taken off on chrome-gelatin films and printed in yellow, blue, and red respectively. Thus three pictures of all that is yellow, blue, or red in the object are obtained. If printed over each other on white paper all the colours of the original object are reproduced.

F. L. T.

Changes of Photographs by prolonged Action of Light. By J. JANSSEN (*Chem. Centr.*, 1881, 159—160).—The author finds that using a gelatin silver bromide plate, the negative image which is formed by an exposure of $\frac{1}{20000}$ second is succeeded by a neutral surface on which a positive image appears at the end of half to one second; on longer exposure this positive is succeeded by another neutral stage, and then a negative makes its appearance again.

F. L. T.

Injurious Effect of Furnace-gases in the Forests of the Upper Harz. By REUSS (*Dingl. polyt. J.*, 241, 285—291).—The following is a summary of the results and conclusions of this interesting investigation (comp. this vol., p. 1064).

The study of the injurious effect of furnace-gases on forests is still in its infancy, but it seems to be established that the gases are injurious mainly on account of the presence of sulphurous acid.

The leaves of all trees absorb a certain quantity of the sulphurous acid, which causes them to become unhealthy, and is followed by the death of separate leaves or branches, or by the complete death of the tree.

Chemical analysis offers the best means of determining the presence of furnace-gases in a district.

The growth of trees in presence of furnace-gases is irregular and variable, but sound strong-looking trees resist their action longer than sickly-looking trees. Deciduous trees, especially the oak, resist the action of the gases better than coniferous trees.

Trees requiring a humous soil rich in mineral constituents cannot flourish in soil impregnated with furnace-gases, the oak being the only exception. Its cultivation in mining districts is looked upon with great expectations. The transformation of forests consisting of diseased coniferous trees into forests with deciduous trees seems feasible in mining districts.

Trees acted on by furnace-gases are not protected against injuries received by insects.

In order to preserve the soil and to maintain its fertility, great care should be taken of it, and it should be kept as dry as possible.

D. B.

Air of Hospitals during Yellow Fever. By W. v. SLOETON (*Chem. Centr.*, 1881, 78—79).—The author determined the free and albuminoid ammonia in the air by Wanklyn, Chapman, and Smith's process. From these analyses, it is shown that the air during the epidemic was laden with albuminoid ammonia, the abnormal amount disappearing with the fever.

F. L. T.

Destruction of Microscopic Animals in Potable Water. By LANGFELDT (*Chem. Centr.*, 1881, 74—75).—The author, in seeking for a substance which would kill the living organisms without injuring the water for drinking purposes, found that citric acid ($\frac{1}{2}$ gram per litre of the water) killed all except *Cyclops* and those with thick epidermis within two minutes.

F. L. T.

Production of Magnesia. (*Chem. News*, **44**, 76.)—Magnesium chloride solution is treated with burnt dolomite. The chlorine combines with the calcium in the dolomite, and in this way magnesia of 98 to 99½ per cent. can be obtained on the large scale without any difficulty. Magnesia bricks prepared with it resist even the oxy-hydrogen flame. In order to separate the sulphate contained in the crude magnesium chloride, calcium chloride is added, and the calcium sulphate thus thrown down is used by paper makers. Magnesia prepared by the above process costs about 15s. per ton. C. H. B.

Magnesia Industry. By T. SCHLÆSING (*Compt. rend.*, **93**, 276—278).—The author proposes to extract magnesium salts from the sea instead of from the saline lakes. The method is as follows:—Magnesia is precipitated from the sea-water by lime, and the gelatinous precipitate obtained is left to settle in large tanks; the clear liquid is decanted off, and the white mud left is converted into the tribasic phosphate by the addition of a calculated quantity of dilute phosphoric acid. The phosphate is allowed to settle, filtered, and converted by the ammonia of sewage into the insoluble ammonium magnesium phosphate. This latter change is based on the fact that the ammonia of sewage, combined with various fixed and volatile acids, in the presence of tribasic phosphoric acid, exchanges one of the equivalents of magnesium for ammonium, whereby the ammonium-magnesium precipitate is formed. This new industry would require the extraction of phosphoric acid from mineral phosphates in the immediate neighbourhood, and the author suggests the working up of human refuse for the extraction of the phosphoric acid. The tribasic magnesium phosphate is not, however, pure, for the original magnesia mud contains 8 per cent. of lime-salts and the phosphoric acid is contaminated with alumina and oxide of iron.

The author considers that among the applications of this proposed magnesia industry will be the manufacture of superphosphates for agricultural purposes, which hitherto have been almost exclusively imported from England. V. H. V.

On Cement (*Dingl. polyt. J.*, **241**, 309; see also this vol., p. 1088).—Schumann has investigated the behaviour of mortar and stone used for building purposes when exposed to the combined action of moisture and air. He found that all cements, if allowed to harden in water, increase in volume, the largest increase being in the first period of the settling. It is larger with newly prepared cement, and smaller with finely ground cement; it is increased when gypsum is added to cement, and decreased when sand is used. As to the action of water and air on stones used for building purposes it is shown that they expand in water, and contract again when dried in the air. The variations in volume decrease with the greater porosity of the stones. Schumann has experimented with a large number of cements and stones, his results leading him to conclude that the changes referred to in the above are too slight to be of any consequence in practice.

Feege mentions that concrete can be exposed to a temperature of

130—150° without influencing its bearing property; however this appears to be the limit. At higher temperatures it loses its firmness and becomes brittle.

From a number of trials made by Schumann on the preparation of mortar, it was found that all cements give the same yield of mortar no matter whether used in the form of a fine or coarse powder or burnt slightly or strongly; he therefore recommends weighing the quantity of cement to be employed instead of measuring it, as is usually the case. Delbrück objects to prepare concrete under water. When it is used for foundations, all excavations should be kept as dry as possible during the actual process of concreting. Büsing and Dyckerhoff, on the other hand, strongly recommend concreting in water. Apart from the fact that to keep large excavations dry for any length of time entails a considerable expense, they show that many large undertakings have been carried out successfully when the concrete was laid in water.

D. B.

Composition of some Cements. (*Chem. Centr.*, 1881, 15).—1. To fill damaged places in castings: 1 part of tar, 1 part rosin are fused together and iron filings stirred in until the mass becomes stiff, it is then allowed to cool. 2. 100 parts rust-free cast-iron borings and turnings are well mixed dry with 1 part coarsely powdered ammonium chloride, and moistened with urine or salt water. No more should be moistened than can be used within an hour. F. L. T.

Explosion of Petroleum and other Combustible Liquids. By R. WEBER (*Dingl. polyt. J.*, 241, 277—285).—The author has investigated the causes of explosions resulting from the products of the distillation of mineral naphtha when used for burning purposes. These products are known as “gasoline,” “benzoline,” “ligroin,” and “lubricating oil.” Some of these are highly inflammable on account of their volatility, a mixture of the vapour with air in certain proportions being very explosive, and accidents have occurred from time to time with fatal consequences. The author’s experiments were made with a view of ascertaining the conditions which were most favourable in preventing these dangerous occurrences. Mixtures of air and carefully prepared gasoline were introduced in various proportions into wide-necked bottles holding 350 c.c., fitted with corks provided with wires. The bottles were kept at definite temperatures for twenty minutes, during which period they were shaken at intervals. An electric spark was then passed through the wires into the bottles. It was found that a mixture prepared with three drops of gasoline produced the most violent explosion, and that as the quantity of this was increased, so the explosive power of the mixture decreased. With six drops of gasoline no explosion ensued. When larger quantities are used the combustion is less perfect, hence the reaction is still weaker, a circumstance which is attributed to the fact that larger quantities of carbonic oxide gas are produced, and that the formation of this gas materially decreases the evolution of heat. Similar experiments were made with carbon bisulphide, the maximum effects being obtained with four drops, ten times this amount being required to produce a

non-explosive mixture. In the case of benzene, two drops gave a violent reaction, four drops gave no explosion. Ether produces a very explosive mixture when four drops are used; with eight drops no explosion takes place. Alcohol gives the maximum effect with five or six drops, but as it is less volatile than ether or benzene it is necessary to heat it. At 30° the explosive action is at its highest, and is reduced both by increasing the temperature—when the gaseous mixture becomes saturated—and by decreasing the temperature when the quantity of vapour given off is not small. D. B.

Formula for Calculating the Quantity of Water Added to Diluted Spirit. By A. ASHBY (*Analyst*, 1881, 1—2).—By using the following formula in conjunction with Hehner's and Stevenson's alcohol tables, the exact quantity of water which must be added to spirit of a given strength to reduce it to any other use may be found.

If x = the volume of water to be added to 100 parts of spirit then the total volume is $100 + x$. and $(100 + x) : 100 ::$ per cent. of alcohol by volume at present strength : per cent. of alcohol by volume at required strength,

$$x = \frac{\text{per cent. of alcohol by vol. at present strength} \times 100}{\text{per cent. of alcohol at required strength}} - 100.$$

By substituting percentage of alcohol by weight for that by volume, the weight of water to be added may be ascertained.

L. T. O'S.

Analyses of Wine and Must. By R. ULBRICHT (*Landw. Versuchs.-Stat.*, 27, 76—100, continued from *Chem. Soc. J.*, 1880, Abst., 586).—In the estimation of sugar, great caution must be observed that all the experiments are exactly alike in the smallest details, in order to obtain comparable and accurate results. Concentration of the sugar solution, absence of sulphur and bodies yielding ammonia on decomposition, temperature of the liquids, &c., are all points demanding careful attention. In endeavouring on these lines to obtain a satisfactory method for the estimation of sugar in must and wine, the author found himself at the outset confronted by several problems still requiring solution. Having prepared a Fehling's solution, the question arose as to how its stability was influenced by temperature, dilution, and difference of composition; 68 experiments on this question were made, and it was found that no copper oxide separated from the solution when diluted to any extent and boiled for ten minutes, if the proportions were those recommended by Fehling, except when the amount of copper present was small, in which cases reduction might be prevented by the use of comparatively larger quantities of Rochelle salt and sodium hydroxide, or by keeping the temperature below 80° C. The smaller the amount of sodium hydroxide present, the greater is the tendency of copper to precipitate, and this is also the case with the Rochelle salt. Friction of the interior of the vessel in which Fehling's solution is heated promotes the separation of cuprous oxide. The presence of ethyl alcohol only caused in concentrated solutions a very slight precipitation of copper, but on the other

hand showed a tendency to retard the reducing agency of dextrose. Glycerol, fats, and thymol gave no results whatever. Fifteen minutes' heating at 70–75°, or ten minutes' at 75–80° was found to be sufficient for the reduction of copper in all the experiments. In concentrated solutions, a moderate increase of the soda in presence of a moderate amount of Rochelle salt increases the reducing power of dextrose with respect to copper; the reverse of this, however, occurs in dilute solutions when the amount of Rochelle salt is small. A greater reduction of copper by a given quantity of dextrose occurs when there is a large excess of copper solution.

In the examination of wines, the author recommends treatment with tartaric acid, then with sodium hydroxide and lead acetate, and finally decolorisation with animal charcoal. After this a rough experiment should be made to ascertain the amount of sugar present, the strength of Fehling's solution used in the final estimation to be fixed accordingly, by a reference to a table given in the original paper.

J. K. C.

Examination of Pressed Yeast. By E. GEISSLER (*Chem. Centr.*, 1881, 158–159).—In the examination of pressed yeast, the author recommends the determination of the yeast, in addition or instead of the determination of starch, ash, and moisture. To determine it, he stirs 3 or 4 grams of the sample in water, dilutes, and heats to complete coagulation, then a few drops of hydrochloric acid are added, and heated until iodine no longer gives a blue with a drop of the fluid. The coagulated yeast is then washed by decantation, finally transferred to a tared filter-paper, dried, and weighed. F. L. T.

The Action of Rennet under Various Conditions. By A. MAYER (*Bied. Centr.*, 1881, 485–491).

Influence of Temperature.—Milk curdles quickest at a temperature of 39°; at 45° it will not curdle, and below 33° the change takes place but very slowly.

Amount of Ferment.—The time of curdling is inversely proportional to the quantity of rennet. The addition of water to the milk retards the coagulation, and the character of the curd is also changed; being naturally gelatinous, it becomes curdy when much water has been added. The natural curdling of milk by "souring" is not affected by dilution. Rich and thin milk curdle in equal times, other conditions being the same.

Motion has no effect on the curdling, except that the curd is gelatinous if the milk is undisturbed. A small amount of heat is evolved during the process of curdling.

Milk from cows of various races, and differently fed, behaves differently with rennet.

Milk coagulates with great difficulty if it has been previously heated to 75°; and as this is the temperature at which milk albumin coagulates, the author shows that this cessation of coagulation is not due alone to the milk albumin, but also to the casein. Heat does not prevent milk from curdling with acids, and 1 per cent. of sodium chloride causes curdling to be more rapid, whereas with 4–10 per cent. it is

slower. Boric acid has but little, whilst potash has much effect in rendering curdling more rapid. The greater the lapse of time after milking, the more rapid is the curdling. Feeble alkalinity, or heating to 66° destroys the action of rennet. Curdling is due to a definite chemical reaction which, when complete, renders the ferment inactive. Among plants, the flower leaves of the artichoke produce the same result as rennet. Bacteria are not necessary to the action of rennet, but, if present, they render it more rapid in its action.

E. W. P.

Milk Analysis. By H. PETER (*Bied. Centr.*, 1881, 482).—It is shown that estimations of the fat in samples of milk may be very erroneous, as, after the milk has been much shaken by travelling, the upper portions in the vessels will contain more cream than the lower, the quantities being in one case 12.3 per cent. above and 2.5 per cent. below.

E. W. P.

Effect of Oxygen on the Quality of Butter. By L. B. ARNOLD (*Bied. Centr.*, 1881, 199—200).—The experiment consisted in placing two portions of milk, each measuring 2 litres, in flasks of double that capacity, filling one flask with oxygen and another with carbonic anhydride, closing them with glass stoppers, and leaving them standing for 48 hours at 17° , at the end of which time the cream had completely separated, and the skim-milk was sour; the latter was withdrawn by a syphon, and the flasks shaken to bring up the butter. In the oxygen flask, the butter commenced to separate after 18 minutes, and was completely removed in 24 minutes; in the carbonic anhydride flask, the butter did not appear till 28 minutes, and finished at 35 minutes. The butter from the oxygen flask had a strong and agreeable aroma, whilst that from the carbonic anhydride flask was insipid and of an oily taste. Both samples were salted and put aside, the keeping property of the former being far superior to the latter. Other samples were allowed to set in the open air, and, both as regards flavour and keeping qualities, occupied an intermediate position between the oxygen and carbonic anhydride samples.

The author concludes that the free access of pure air to the milk during the process of creaming is most essential to the production of the best qualities of butter.

J. F.

Ripening of Cheese. By G. MUSSO and others (*Bied. Centr.*, 1881, 201—203).—The quantity of water retained by fresh cheese after working and pressing, is considerable, and varies greatly; it depends, according to the authors, on the mechanical manipulation of the milk during and after coagulation. Milk which is agitated during the addition of the rennet and until the coagulum separates, when pressed will retain 45 per cent. of water; the same milk, suffered to remain at rest during the process, will, after pressing, contain 79 per cent. of water, only removable by drying. The constituents of fresh coagulum of milk are enumerated as fat, albuminoid substances, milk-sugar, lactic acid, mineral substances, soluble and insoluble in water; peptones, amides, ammonia, free and combined fatty acids. The first change which takes place in the freshly-made cheese is in the

albuminoid substances existing as a kind of double calcium and phosphorus salt. The formation of organic acids withdraws a portion of the lime, forming compounds readily soluble in water, as may be proved from the quantity of calcium salts found in the aqueous extract of all kinds of ripe cheese. The true albumin does not appear to diminish during the process of ripening. The author examines the process by which milk-sugar is formed: first by a sort of mucous fermentation; the fluid which drops from Parmesan cheese is slimy, thick, and ropy; secondly, by alcoholic fermentation, which is sometimes perceived during the heat of summer; two samples of 500 grams each, of a two days' old cheese, contained 2.44 and 3.71 grams alcohol and 0.39 and 0.66 gram of acetic acid; thirdly, through lactic and butyric fermentation. J. F.

Use of Salicylic Acid in the Dairy. By K. PORTELE (*Landw. Versuchs.-Stat.*, **27**, 143—149).—Salicylic acid cannot be directly estimated in milk if the quantity is less than 50 g. per hectolitre, but by evaporation of the milk to dryness and extraction with ether, the presence of still smaller quantities can be ascertained. Given along with fodder, it makes its reappearance shortly in the milk and urine, but disappears after some hours in the former, not showing its presence again, although large quantities may be mixed with the food. It does not act satisfactorily as a preservative of either milk or butter, giving them an unpleasant sweetish taste, increasing in strength until decomposition sets in. A weak solution painted over the surface of cheeses will however preserve them from the white mould often visible after they have been kept for a few months. J. K. C.

A Cause of Alteration of Textile Fabrics. By BALLAUD (*Compt. rend.*, **92**, 462).—Some linen sheets, which had a slight brown colour, were noticed to have dark spots on them after washing in ordinary carbonate of soda. These spots partly disappeared on drying, and the stuff fell into holes at the spots.

The linen had been washed with dilute solution of sulphate of iron and then with lime. Oxide of iron was thus deposited in the tissue, and on coming into contact with the sulphides in the washing soda, sulphide of iron was formed, which then oxidised to sulphate.

Calicoes dyed or printed by means of iron salts sometimes fall into holes by the alternate oxidation and reduction of the iron in the tissue. C. W. W.

Use of Cadmium in Calico-printing. (*Dingl. polyt. J.*, **241**, 149).—At the present time cadmium can be procured at a moderate price, although hitherto it has been too costly for profitable use in calico-printing. According to Jaquet, however, both chlorine and light act on cadmium-yellow. Schmid employs cadmium nitrate, which is converted into the sulphide by treatment with sodium thiosulphate. He obtains a steam-yellow with starch in the following manner:—1 litre water, 160 grams wheat-starch, and 40 grams burnt starch are boiled together and treated, whilst hot, with 350 grams sodium thiosulphate. When cold, 350 grams of finely-crushed cadmium nitrate are added. A better result is obtained when sodium thiosul-

phate is replaced by arsenious acid and sodium acetate, the latter forms the solvent for sulphur, and is said to better fix the cadmium-yellow. Jaquet mentions that chrome-yellow and chrome-orange in steaming resist the action of sulphuretted hydrogen perfectly when 30 to 40 grams cadmium nitrate and 10 to 20 grams sodium acetate are added to 1 litre of printing colour.

D. B.

Preparation of Aniline Black. By C. GLENCK (*Dingl. polyt. J.*, 248, 234).—In place of potassium chlorate, the chlorates of sodium and barium, although more costly, are now largely used, on account of their greater solubility in water, which enables manufacturers to use larger quantities. Thus stronger solutions are obtained which do not deposit crystals of chlorates in the colour, and the formation of streaky colours is prevented. 1 litre water dissolves about 60 grams potassium chlorate, 275 barium chlorate, and 1000 sodium chlorate. Potassium chlorate contains 61·5 per cent. chloric acid, barium chlorate 49·5 per cent., and sodium chlorate 70·6 per cent.

For the preparation of steamed aniline black, the use of barium chlorate is recommended. If, however, sulphates are present, sodium chlorate must be used in the preparation of colours, as the sulphate of barium produced weakens the lustre of the colours, and retards the printing process; moreover, the stability of the colour is altered.

D. B.

New Observations in Tanning. By K. SADLON (*Dingl. polyt. J.*, 240, 228—231).—The author mentions that the most important defect in tanning is that only two-thirds, and often only one-third, of the real tannin substance is utilised, whilst the remainder is wasted. The first condition necessary for effecting a rational extraction of the total tannin contained in the material used is the employment of an elevated temperature. Thus the cells of the material used are softened more quickly and perfectly, the diffusion is accelerated, and the solvent power of the water increased so that concentrated solutions are obtained and larger proportions of the insoluble modification of the tannin dissolved. The only objection raised against hot extraction is that the colour of the leather tanned with such extracts is always darker. However, this can be easily overcome by cooling the extract before the skins are introduced. It was found that on cooling to 18°, large quantities of a yellowish-brown precipitate were deposited, consisting chiefly of the insoluble modification of tannin, oak phlobaphene, as in this case oak-bark had been used, but the same precipitate was obtained with other tannins. The author tried a series of experiments with a view of obtaining a solvent for this precipitate. Sodium borate was found to give the best results. By treating the tannin material with warm water containing 0·5 per cent. borax, a very strong extract is obtained, which, on cooling, no longer deposits any precipitate. Moreover, the durability of the extract is increased considerably, and the time required for tanning skins with this extract is greatly reduced. Fresh skins were treated with this extract, no shrinking was visible, the external and internal layers maintained their natural character, the skins remained soft, and the pores open.

D. B.

ERRATA IN VOL. XL.

Page.	Line.				
98	7 from bottom	for $C_9H_5NO_4 + H_2O$	read $C_9H_5NO_4 + H_2$.		
102	18	„ „	$C_{40}H_{82}O_{19}$	„	$C_{48}H_{82}O_{19}$.
102	7	„ „	$C_{10}H_{13}O$	„	$C_{10}H_{18}O$.
418	last line	„	ferrocyanide	„	ferricyanide.
419	2 from top	„	ferrous	„	ferric.
778	2 from bottom	}			
779	26 from top		„ <i>Ann. Chim. Phys.</i>	„	<i>Ann. Phys. Chem.</i>
783	13 „				
966	19 from top	„	(<i>i.e.</i> , lower by 124°)	„	lower (namely at 124°).
968	17 from bottom	„	Ag_5IBrCl_2	„	Ag_5IBrCl .
1057	21	„ „	urine	„	urobilin.
1057	26	„ „	and not with	„	and with.